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Colophon

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Synopsis

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An exploratory study

Steelworks make steel from crude iron and steel scrap. Steel scrap can contain contaminants, such as rust-resistant primer with chromium (VI). The Ministry of Infrastructure and Water Management (I&W) asked RIVM to estimate how much chromium(VI) steel production processes emit into the atmosphere when this paint is present on scrap. It also asked RIVM to compare this figure to the quantity emitted from scrap without this paint. Since 2017, chromium (VI) is no longer permitted in paint because it is harmful to health.

The quantity of chromium(VI) in steel scrap treated with primer containing chromium(VI) varies widely. According to RIVM's estimates, there is an average of 0.03 per cent chromium(VI) in that steel scrap. It is not known how much steel scrap in the Netherlands has been contaminated with paint containing chromium (VI). This means our estimate (around 1 per cent of the total quantity of scrap processed) is uncertain.

The amount of chromium(VI) emitted largely depends on where the chromium(VI) from steel scrap ends up during steel production. If it is left in with the crude iron and molten steel scrap, it largely ends up in the steel or steel slag. It can also mainly be released as dust particles, when the hot metal is poured over the scrap in the steel furnace. Part of the dust particles are captured, while the rest enter the air inside the production hall, from where they travel to the outside air.

RIVM has therefore worked out ratios in various scenarios, along with the consequences for emissions. In the molten steel scenario, emissions of chromium(VI) are a few dozen per cent higher than for scrap without this paint. When released as dust particles following the pouring-over of hot metal, the emissions may be much higher than for scrap without chromium(VI).

It is not only through paint that chromium(VI) can end up in emissions. Chromium can also be found in steel scrap in metallic form, and in the raw materials for steel production. Chromium can partly be converted into chromium(VI) during the production process.

Due to the harmful properties of chromium(VI), RIVM recommends measuring how much is present in particle form in indoor air and how much is emitted to the outside air. RIVM also recommends working out how much steel scrap containing chromium(VI) is available for recycling in the Netherlands and where it has been processed in the past. A lot of steel scrap from the Netherlands is sold abroad.

Keywords: recycling, steel scrap, steel production, paint containing chromium (VI), chromium (VI) emissions, chromium (VI) exposure

Publiekssamenvatting

Mogelijke emissie van chroom-6 tijdens de verwerking van staalschroot met chroom-6 houdende verf.

Een verkenning

Staalfabrieken maken staal van ruwijzer en staalschroot. Staalschroot kan vervuilingen bevatten, zoals roestwerende grondverven met chroom-6. Het ministerie van Infrastructuur en Waterstaat (IenW) heeft het RIVM gevraagd in te schatten hoeveel chroom-6 staalfabrieken naar de lucht uitstoten wanneer deze verf op het schroot zit. Dit is vergeleken met de hoeveelheid bij schroot zonder deze verf. Sinds 2017 mag er geen chroom-6 meer in verf zitten, omdat deze stof schadelijk is voor de gezondheid.

De hoeveelheid chroom-6 in het staalschroot dat is behandeld met grondverf met chroom-6, verschilt sterk. Volgens schattingen van het RIVM zit er gemiddeld 0,03 procent chroom-6 in dat staalschroot. Het is niet bekend hoeveel staalschroot er in Nederland is waar verf met chroom-6 op zit. Dat maakt onze schatting daarvan (rond de 1 procent van de totale hoeveelheid verwerkte schroot) onzeker.

Hoeveel chroom-6 wordt uitgestoten hangt sterk af van waar het chroom-6 van verf in staalschroot tijdens de productie van staal terechtkomt. Wanneer dat in het ruwijzer en het gesmolten staalschroot blijft, zal het grootste deel in het staal of de staalslakken eindigen. Daarnaast kan het ook vooral met stofdeeltjes vrijkomen wanneer in de staaloven het ruwijzer over het schroot wordt gegoten. Een deel daarvan wordt afgevangen, de rest komt in de binnenlucht van de productiehal en de buitenlucht terecht.

Het RIVM heeft daarom in verschillende scenario's uitgewerkt hoe deze verhoudingen liggen en wat de gevolgen daarvan zijn voor de uitstoot. In het scenario van het gesmolten staalschroot is de uitstoot van chroom-6 tot enkele tientallen procenten groter dan bij schroot zonder verf met chroom-6. Wanneer het vrijkomt met stofdeeltjes bij het overgieten, kan de uitstoot veel groter zijn dan bij schroot zonder deze verf.

Chroom-6 komt niet alleen via verf in de uitstoot terecht. Chroom zit ook als metaal in het staalschroot en in de grondstoffen voor staalproductie (zit in ijzererts). Tijdens het productieproces kan dat voor een deel worden omgezet in chroom-6 en in de uitstoot komen.

Vanwege de schadelijke eigenschappen van chroom-6 beveelt het RIVM aan te meten hoeveel ervan in het stof in de binnenlucht van staalfabrieken zit en naar buiten wordt uitgestoten. Ook beveelt het RIVM aan om uit te zoeken hoeveel staalschroot met chroom-6 in Nederland beschikbaar komt voor recycling en waar dat wordt verwerkt. Veel Nederlands staalschroot wordt namelijk verkocht aan het buitenland.

Kernwoorden: recycling, staalschroot, staalproductie, Chroom-6-houdende verf, chroom-6-emissie, chroom-6-blootstelling

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Summary

Introduction and aim

Integrated steel plants obtain the iron they use for the purpose of producing steel (i.e. primary steel production) from iron ore and steel scrap. Steel scrap can contain contaminants, one of them being chromium(VI), which has been used as a rust-inhibiting agent in coatings for steel. Chromium(VI) is a carcinogen and exposure may have harmful effects on human health. In the Netherlands, questions were raised on whether there is a need to prevent chromium(VI) coated steel scrap from being processed in common steel production plants (anywhere in the world), in regard of harmful emissions of chromium(VI) that were supposed to occur from processing the scrap. The Ministry of Infrastructure and Water Management in the Netherlands therefore requested RIVM to perform a study to estimate how relevant these emissions could be. Based on the results the Ministry decides on further actions.

The main question was to what extent the processing of steel scrap with paint containing chromium(VI) leads to additional emissions of chromium(VI) into the indoor air and outside air compared to clean steel scrap. The purpose of this analysis is to gain insight into the emissions of total chromium and chromium(VI) in the primary steel production and the potential reduction of these emissions if only steel scrap *without* paint that contains chromium(VI) were to be used.

Chromium VI paint on steel

The first step was to investigate what are the measured or expected concentrations of chromium(VI) in the paint layers on steel. The second step was to quantify the amount of chromium (total and chromium(VI)) present in steel scrap with paint layers containing chromium(VI) and in the total amount of Dutch steel scrap.

In the past chromium(VI) was added to rust-resistant primers, mostly strontium chromate and zinc chromate. It was also used as a pigment in top coats. Measured concentrations of chromium(VI) in chromium(VI) containing paints average around 1,000 to 3,000 mg per kg of dry paint, with a range of 20 mg per kilogram up to a maximum of 10,000 mg per kg of dry paint. Calculated concentrations in the primer are in the range of 40,000 mg per kg (dry paint) for zinc chromate and around 100,000 mg per kg (dry paint) for strontium chromate. For the entire paint layer, the concentrations range from 7,000 to 20,000 mg per kg of paint. The calculated concentrations are in general higher than the measured concentrations. This can be explained by the fact that during the lifespan of painted objects part of the chromium(VI) is reduced to trivalent chromium(III) or that a portion of the paint has been removed and replaced with chromium(VI)-free coatings or that additional chromium(VI)-free paint layers are applied on top of the existing intact layers.

Calculated concentrations of chromium(VI) based on the mass of the steel product, resulting from newly applied paint have an average of about 300 mg/kg (0.03%) with a range of 200-900 mg/kg for sheet material and 80-200 mg/kg for light and medium-weight construction beams. These concentrations for steel treated *with chromium(VI)* paints are in the same order of magnitude as the content of *total chromium* in well-sorted unalloyed steel scrap (0,05%). The estimated average chromium(VI) content of 300 mg/kg is high considering the measured values in paint layers on scrap, which are about a factor of eight lower than the calculated values.
A first uncertain indication of the percentage of the total quantity of scrap processed in the Netherlands that might contain chromium(VI) is 1 percent. This fraction is used for the scenario calculations.

Air emissions of chromium and chromium VI from steel plants

With regard to the emissions, in this study we focus on the primary (or integrated) steel production process applying the blast furnace process followed by the basic oxygen furnace (BOF) steelmaking process. Furthermore, we consider chromium emissions during secondary steel production using electric arc furnaces (EAF) and emission occurring from induction furnaces and EAFs that are used by foundries.

There is no emission data on chromium(VI) available with regard to primary and secondary steel production. Similarly, virtually no information is available regarding the presence of chromium(VI) in the dust that is formed and emitted. The BREF for the iron and steel industry does mention the possibility of chromium(VI) emissions. Yet no additional (quantitative) information is included.
Emissions will primarily be released into air. Emission to water may also occur through wet flue gas scrubber techniques, but appears to be limited.

For steel foundries, generally the quantity of dust generated by the use of induction ovens is 10 times lower than that generated by EAFs. Within the (secondary) steel production, the amounts of dust generated by EAFs and BOFs are comparable. The dust emission from EAFs used by foundries are about a factor of three lower compared to steelmaking. Emissions of total chromium to air from the BOF process are in the range of 0.01 to 0.075 g per ton steel. The emission of total chromium to air of the BOF process is more or less comparable to that of induction furnaces. This is largely due to the fact that, although the dust emissions in the BOF process are higher, chromium content of the dust generated by the BOF process compared to the induction furnaces is lower. The chromium concentrations for dust found in the literature, however, are very uncertain (especially for induction furnaces) and show a wide range of values.

Chromium(VI) emissions originating from the coatings on scrap are expected to occur primarily during steelmaking when the scrap is charged into the furnace and when the hot metal is charged and poured on the scrap. Based on the description of how dust emissions are formed during steel production, the expectation is that the majority of that dust will end up in the flue gas and not in the molten steel bath. The degree

to which the emitted chromium(VI) will be captured depends mostly on the efficiency of the secondary and potential tertiary flue gas treatment system. The expectation is that it is possible to capture around 80% (secondary treatment) and up to 90% (secondary plus tertiary treatment) of those emissions in BOF-steelmaking.

Chromium balance in the steel production

In the primary steel production process the *total input of chromium* in the steel originating from raw materials is estimated at about 130 g per ton of steel (range 80 to 240 g). These values apply to a situation in which the removal of chromium through slag is taken into account. Based on available data, it is assumed that 50% is removed via blast furnace slag and 55% is removed via slag in the BOF. If no removal through slag is assumed, the calculated chromium content will be approximately 330g per ton of steel. The major sources of chromium in steel are iron ore and scrap. According to the calculations, scrap accounts for approximately 75% of the chromium entering the process. There is some uncertainty in the removal of chromium in the blast furnace. Some data suggest that the removal is less, about 10%. In the secondary steel process, scrap accounts for virtually 100% of the presence of chromium.

Another question was where the *chromium from the input sources ends up.* (output to flue gas treatment residues, emitted fine and other particulate matter, waste/drainage water, newly produced steel) Based on the mass-balance approximately 50% of the chromium present in the raw materials will end up in the slag formed during the BOF process. The remaining portion will end up in the steel being produced. A small quantity is present in the collected dust (less than 1%) and less than 0.1% is expected to be emitted into the air. Usually collected dust is recycled back into the production process and should therefore not be considered as losses. The total quantity of chromium emitted to air is in the range of 0.010-0.075 g of chromium per ton of steel.

Formation and conversion of chromium VI

The information found in the literature is ambiguous with regard to the potential formation of chromium(VI) in slag during the production of primary steel. A considerable number of studies demonstrated the formation of chromium(VI) in slag. On the other hand, there is a study concluding that formation of chromium(VI) would not occur. Recent measurement data, however, show that there is chromium(VI) present in the slag formed during the BOF process in an amount of around 0.5% of the total quantity of chromium. Little information is available on the chromium(VI) content in emitted dust. One study found that the fraction of chromium(VI) in dust accounts for 0.25% of the total chromium (during stainless steel production).

What happens to the chromium(VI) from coatings during the BOF process depends on how it is released and where it ends up in the process. Chromium(VI) entering the process might end up in the dust formed during the process, in the molten steel bath or the steel slag. The portion that ends up in the dust being formed is expected not to be

reduced to trivalent chromium. A substantial part of the chromium(VI) present in the coatings might end up in the generated dust, but this is uncertain. Another part will end up in the slag and be mostly reduced, depending on the process conditions. The part that ends up in the steel bath will likely be reduced in its entirety.

Scenarios on Chromium(VI) emissions to outside air

To discuss the importance of chromium(VI) emissions to in the BOF-process air from scrap containing chromium(VI) paints compared to a reference without chromium(VI) paints, four scenarios (A, B, C and D) for potential chromium emissions were described. Chromium can also be found in metallic form in steel scrap and in the raw materials for steel production. Also in the reference situation to some extend chromium can be converted into chromium(VI) during the production process. The calculated ratios give an indication of the potential relevance of additional chromium(VI) emissions to air.

Scenario A. This scenario compares the emission situation assuming that the chromium(VI) from paint (coatings) will be distributed across the steel, slag and emissions to air in the same way as the total chromium (lower bound paint scenario), to the lower bound reference emissions. The extra contribution from paint containing chromium(VI) is an increase by a factor 0.2 in comparison to the reference emission.
In scenario B. we also take the lower bound paint scenario (as in scenario A). However, we compare it to the higher bound reference emission. This scenario shows a marginal increase (factor 0.02 higher) in chromium(VI) emissions due to steel scrap containing chromium(VI) paints.
In scenario C we compare the upper bound paint scenario to the lower bound baseline emissions. The upper bound paint scenario assumes that 10% of the quantity of chromium(VI) in paint will be emitted to the outside air. The underlying assumption is that all the chromium(VI) in paint on the scrap is released to air during the scrap and hot metal charging. 90% of the chromium(VI) released is captured by emission-control equipment. This comparison reveals that the chromium(VI) emissions might increase about a factor of 300.
In scenario D the upper bound paint scenario is compared to the upper bound reference emission. From this ratio it appears that the chromium(VI) emissions might increase about a factor of 30.

The scenarios show that there is a high degree of uncertainty regarding the diffuse emissions during the process of loading steel scrap into the converter. It is still unclear which portion of the chromium(VI) ends up in the bath and which portion ends up in the dust emissions. The fraction of the dust that is released during the most critical step, the loading of hot metal, varies from 6 to 11%. An additional tertiary capture system could reduce these 'rooftop' emissions. It is also unclear if the chromium (VI) in paint ends up in the molten bath of the converter, to which extent it will be converted to chromium(III) or metallic chromium. Because of these uncertainties the outcomes should be used with care.

Main conclusion

It was concluded that chromium(VI) emissions are highly dependent on what happens to the chromium(VI) in paints during charging of steel scrap and the subsequent pouring of the hot metal on the steel scrap in the primary steel production process (BOF). When the chromium(VI) present in paints is distributed in the same way as the chromium present in the hot metal and steel scrap (lower bound paint scenario), additional emissions due to scrap with paints will be in the same order of magnitude as in the reference scenario . When it is assumed that the amount of chromium(VI) from paint present in the scrap is released during steel scrap charging, emissions of chromium(VI) from paint may be two orders of magnitude higher than chromium(VI) emissions in the reference scenario.

Diffuse indoor emissions during loading of the scrap might also lead to exposure of workers due to inhalation.

It should be considered that the estimated average chromium(VI) content of 300 mg/kg in scrap is higher than the measured values in paint layers (average is a factor of eight). This means that above mentioned ratio of emissions of chromium (VI) can be seen as maxicould be lower.

The estimated emissions of total chromium from the BOF process are expected to be higher than those from the use of induction furnaces in the steel melting process (foundries). Without emission-control measures, the emissions to air may differ by a factor of 10. Chromium emissions are highly influenced by the scrap quality and the degree of emission control.

Recommendations

We recommend conducting measurements to gain further insight into dust emissions and the presence of chromium in dust during the loading of scrap and molten iron in the primary steel production process. Because the scrap loading and the pouring of the hot metal only happens within a limited time span (5-10 minutes), it is recommended to focus on collection of dust on these moments in the air near the process to be able to estimate relevance for workers exposure to chromium(VI).
We also recommend to analyse the ratio between total chromium and chromium(VI) in captured dust. It is also recommended to measure the chromium(VI)-content in the dust coming from the primary, and secondary abatement systems. This gives an indication of the relevant environmental exposure.
We recommend generating insight into the material flows of steel with chromium(VI) paint in the Netherlands. This could consist of an inventory conducted by the managers of objects and equipment suspected to contain chromium(VI), such as TenneT, ProRail, Rijkswaterstaat, the Central Government Real Estate Agency, Dutch Railways, the Ministry of Defence and scrap processors. Another possibility would be to perform a historical assessment on the use of primers with chromium(VI) in the Netherlands. This could give insight in where paints might still be present. In addition an investigation is

recommended on the destination of steel scrap to get insight in the total amount and potential location of emissions. This should be done in cooperation with the 'Human Environment and Transport Inspectorate'.

1   Introduction

1.1   Context and purpose

Integrated steel plants obtain most of the iron they use for the purpose of producing steel (i.e. primary steel production) from pig iron derived from iron ore. The other raw material used is steel scrap. Some steel production processes rely almost entirely on the use of steel scrap (i.e. secondary steel production). There are also more specialised foundries where virtually the entire operation is dedicated to recycling steel scrap or using pig iron in combination with steel scrap.

Steel scrap can contain contaminants, one of them being Chromium(VI) – also known as hexavalent chromium –, an oxidation state of the metal chromium. Chromium(VI) has been used as a rust-inhibiting agent in coatings for steel. In this report, we will use the notations 'chromium(VI)'. Exposure to chromium(VI) may have harmful effects on human health. It can result in medical conditions such as cancer and chronic pulmonary disease.
In the Netherlands, questions were raised on whether there is a need to prevent chromium(VI) coated steel scrap from being processed in common steel production plants (anywhere in the world), in regard of harmful emissions of chromium(VI) that were supposed to occur from processing the scrap. The Ministry of Infrastructure and Water Management (IenW) in the Netherlands therefore requested RIVM to perform a study to estimate how relevant these emission could be. Based on the results the Ministry will consider whether it is desirable to enact measures aimed at controlling emissions resulting from the recycling of steel scrap containing chromium(VI) from paints.

The purpose of this study is therefore to determine the extent to which the environmental impact of steel plants will change in the event these factories cease to process scrap with paint containing chromium(VI). This does not pertain to a specific steel plant, but rather to steel production in general. If this should prove to be the case, it can then be explored whether and what type of measure should be taken to make a significant improvement to the environmental aspect.
Because paint layers can also contain other heavy metals, particularly lead, this was also part of the research question. Due to the quantity of data required, the scope of this stage was limited to total chromium and chromium(VI).
Steel scrap containing chromium(VI) is not currently considered to be hazardous waste. One reason for this is the assumption that the percentage of chromium(VI) in steel coated with chromium(VI) paint does not exceed 0.1%, which is a threshold within the classification as hazardous waste [1].

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[1] Handreiking EURAL | Brochure | Rijksoverheid.nl

1.2   Main question

We have formulated the research question to be answered as follows: With regard to primary and other steel production, how do potential emissions of chromium(VI) into air, resulting from the processing of steel scrap containing chromium(VI) from paint relate to the total emissions of this metal?

Sub-questions:

1. What are the measured or expected concentrations of chromium(VI) in the paint layers on steel?
2. What are the anticipated emissions of chromium(VI) into the air (and, where possible, those into water and in waste flows) from various types of steel plants (per ton of produced steel)?
3. What is the range for quantities of chromium (total and chromium(VI) in the primary raw materials of steel (per ton of produced steel)?
   a. Iron ore
   b. Coke
4. What quantity of chromium (total and chromium(VI) specifically) is present in steel scrap in the following component:
   a. Paint layers containing chromium(VI).
   b. The bulk of the steel scrap.
5. Where does the chromium from these sources end up? (flue gas treatment residues, emitted fine and other particulate matter, waste/drainage water, alloying with newly produced steel, and so on)[2]?
6. What is known about the formation and/or conversion of chromium(VI) during primary and secondary steel production?

The purpose of this analysis is to gain insight into the relationship between the potential existing emissions of total chromium and chromium(VI) as a result of primary steel production and the potential reduction of these emissions if only steel scrap *without* paint that contains chromium(VI) were to be used. To that end, it is also relevant to summarise the knowledge from literature which pertains to the conversion of chromium(VI) from paint or the formation of chromium(VI).

In case this investigation reveals that the use of steel scrap with paint containing chromium(VI) can lead to a considerable increase in emissions, it would be desirable to explore the emissions and production processes in greater detail in the follow-up stage, as well as take a closer look at how serious the environmental impact of these additional chromium(VI) emissions is.

1.3   Approach and reader's guide

To answer the questions above, a number of steps were taken to gain an idea of the relevance of chromium(VI) emissions resulting from the processing of steel scrap in the primary steel production process. Prior to these efforts, the extent of the available data on chromium(VI)

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[2] Answering sub-question 5 requires knowledge of (among other things) how chromium(VI), other forms of chromium and other heavy metals behave in the various consecutive steps of the process that take place at a steel plant (blast furnace or other furnace type), from the moment of arrival to the cooling of the produced steel.

emissions and composition was unknown. The approach therefore initially focused on answering questions 1–6. Using the resulting information, an analysis was conducted for the purpose of answering the main question.

First, the available literature was reviewed to learn how much chromium(VI) can potentially be present in steel scrap. To do so, we first looked at concentrations in paint and then estimated the concentrations resulting from the presence of such paint in steel scrap (*questions 1 and 4*). This is described in section 2.

Secondly, the mass balance of the input and output of materials in the primary steel production process has been described based on the literature and the registration of emissions. Based on the content in these materials, we have estimated the quantities of total chromium that enter and are released by the primary steel production process in the form of products, waste flows and emissions. Total chromium is also relevant because metallic chromium and chromium(III) can be converted to chromium(VI). Where possible, it was explored whether (in addition to data on total chromium) data was also available on the presence of chromium(VI) in materials (raw materials and waste flows) and emissions. In section 3, the available information is used to compile a chromium balance (*questions 2, 3 and 5*). A similar balance has been drawn up for secondary steel production as well.

Thirdly, based on the literature, specific effort has been made to explore the available knowledge with regard to the conversion and creation of chromium(VI) during the course of primary and secondary steel production (section 4). Scenarios have been drawn up using the available data. This made it possible to estimate the potential emissions into the air of chromium(VI) as a result of processing steel scrap with paint containing chromium(VI), as compared to the amount of total chromium and chromium(VI) currently being emitted during (primary and other) steel production, i.e. the reference scenario. The ratio between the two gives an idea as to the relative significance of potential additional chromium(VI) emissions (section 5).

Lastly, conclusions will be drawn and recommendations made for possible supplementary action (section 6).

2   Presence of chromium and chromium(VI) in steel scrap

2.1   Introduction

This section addresses the chromium(VI) found in corrosion-resistant paints used on steel. It focuses primarily on answering the research questions 1, 4a and 4b. First, the legislation related to chromium(VI) is briefly addressed (see 2.2). The quantity of chromium(VI) present in corrosion-resistant paint is examined, and from this the quantity that is applied to the surface being painted. This information is used to estimate the potential chromium(VI) content of scrap with regard to painted steel construction materials (see 2.3). The primary source for this is the product information of paints containing chromium(VI), as well as information which was collected about the concentrations measured in painted objects. Lastly, the question of the total amount of chromium(VI) that can potentially be present in iron and steel scrap is addressed (see 2.4). To answer this question, a literature review was conducted of studies in which the chromium content of scrap metal was measured. The final step consists of an estimate of the percentage of steel scrap that contains chromium(VI) (see 2.5).

2.2   The metal chromium and relevant legislation and regulations

Chromium is a silver-coloured metal. In addition to its metallic form, chromium also exists in various oxidation states. The two most common and stable forms are trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) chromium. Other valencies such as bivalent (CrO) and tetravalent (CrO_2) may exist as well. Trivalent chromium is an essential nutrient for metabolic processes in the human body.

Chromium(VI) – Cr6 – is a toxic form of chromium. It is classified (among other things) as a carcinogen and mutagen for humans and as highly toxic for aquatic organisms [ECHA, 2022a]. Most compounds containing chromium(VI) are classified as such. This now also applies to barium chromate as well, which previously lacked a harmonised classification. Currently, there is a proposal under consideration which calls for the inclusion of this substance in Annex VI of the CLP Regulation [ECHA, 2022b]. Annex VI is the list of harmonised classifications and labelling for hazardous substances according to the criteria set out in the CLP Regulation.

Due to these hazardous qualities, the majority of chromium(VI) compounds – including strontium chromate and zinc chromate) have been designated by the REACH Regulation as substances of very high concern (SVHCs). A large portion of these compounds have been included on the list of substances (Annex XIV) for which authorisation is required under the terms of the REACH Regulation. This means that companies must obtain authorisation from the European Commission in order to continue working with these substances. In the long term, the new harmonised classification system will make it possible to add barium chromate to Annex XIV of the REACH Regulation as well. Chromium(VI) compounds are also listed in Annex XVII (entry 47) of the REACH Regulation. Annex XVII establishes which substances are subject

to certain usage restrictions. The restrictions on chromium(VI) set out in Annex XVII of the REACH Regulation pertain to its use in cement and its presence in leather.

According to Dutch emissions policy, chromium(VI) and all chromium(VI) compounds are considered to be substances of high concern (in Dutch, zeer zorgwekkende stoffen, which is abbreviated as ZZS). This means that the emissions policy for ZZS applies to all compounds containing chromium(VI). One provision of that policy requires companies to prevent ZZS from being released into the air and water. When this is not feasible, they must take step to limit the emissions to an absolute minimum (minimisation obligation).

LAP3 sets out the policy for handling waste that contains a ZZS. A company must conduct a risk analysis if it wants to put waste material containing a ZZS to productive use and when determining the final stage of the waste processing. This risk analysis must show that there are no unacceptable risks in connection with the intended use of that material. Waste is classified as 'waste that contains a ZZS when the concentration of the ZZS present exceeds the limit value established in LAP3 [IenW, 2021]. During the collection and processing of waste, some mixing may occur. Before the mixing of waste materials and ZZS is permissible, there must be an assessment based on comparison to the minimum standard and the mixing policy set out in LAP3. It must additionally be established that the processing is not in violation of REACH or POP regulations and/or the policy guidelines for ZZS [IenW, 2021].

2.3 Chromium(VI) on painted steel

This sub-section deals with the quantity of chromium(VI) present in corrosion-resistant paints and the quantity that is applied to the surface being painted. The chromium(VI) content of scrap will be estimated with regard to various painted steel construction materials. A study was also conducted of the measured values of chromium(VI) in old and existing paint layers. Sub-section 2.4 explains how much chromium (total) and chromium(VI) can potentially be present in iron and steel scrap. To answer this question, a literature review was conducted of studies in which the chromium content of scrap metal was measured and the specifications for various types of scrap metal were reviewed.

2.3.1 Chromium(VI) in paint

In order to protect metals from corrosion, it is necessary to create a barrier between the metal and the surrounding environment. A common method for achieving this is to apply a coating. For functional and aesthetic reasons, the applied paint actually consists of multiple layers, which are collectively referred to as a 'paint system' or 'coating system'. A paint system may be comprised of the following types of paint, each with its own specific function and characteristics:
- Primer: this is the first layer, which ensures that subsequent layers will adhere properly to the surface. Corrosion-resistant pigments are added for their corrosion-resistant properties.
- A sealer is used as an intermediate layer in a coating system in order to increase the total protection and to ensure a proper

bond between the individual layers of paint. Sealants are
generally applied on porous surfaces.
- The fill layer or build coat is an intermediary layer that is applied
in order to achieve thicker layers and therefore provide greater
protection for the underlying surface.
- The finishing layer or top coat gives the coating system its
desired colour, shine and surface resistance.

Certain paints can be used to serve multiple purposes, for instance
functioning as both fill layer and finishing layer. To obtain specific anti-
corrosive qualities, however, primers with corrosion-resistant additives
are almost always used. These primers are then painted over with one
or more layers.

Especially in the past, paints containing chromium(VI) were used to
protect steel and aluminium against corrosion. Over time, due to its
harmful effects on human health, chromium(VI) has gradually been
replaced by chromium(VI)-free alternatives such as zinc phosphates and
zinc oxide. The transition to chromium-free paint systems began in the
late 1980s. It was motivated in part by the classification of paints
containing chromium as carcinogenic, mutagenic and reprotoxic (CMR)
and by the availability of chromium-free alternatives [Van der Meer et
al., 2022]. Geraets et al. [2020] similarly indicate that the widespread
use of chromium(VI) in paints and coatings was halted in the late 1980s
and early 1990s. In certain sectors (such as the military and aviation
industries), however, it is still applied to protect surfaces against
corrosion [Geraets et al., 2020]. This is evident in the inventory of
authorisation requests submitted by Dutch businesses which was
conducted by Geraets et al. [2020]. Aside from the fact that most of the
requests for authorisation to use chromium(VI) in coatings were
submitted for applications in the aviation and defence sectors, it was
also revealed that a Dutch company submitted authorisation requests
for applications as colour pigment in coatings for metal objects and for
surface markings on roads and at airports [Geraets et al., 2020].

Chromium(VI) in primer coats
Various salts containing chromium(VI) may be added to a primer to lend
it corrosion-resistant properties. These are typically lead chromate,
strontium chromate, barium chromate and zinc potassium chromate
(found in yellow 36 and other pigments). Strontium chromate is used
primarily on aluminium but may also be used on steel. Zinc potassium
chromate is applied mainly to steel.

Chromium(VI) in top coats
Lead chromate ($PbCrO_4$) was previously used as a yellow pigment due to
its yellow hue and rust-resistant qualities. In the 1970s, Dutch Railways'
train cars were spray-painted yellow using paint that contained lead
chromate. To a lesser degree, lead chromate is also incorporated into
certain types of red and orange paint [Van der Meer et al., 2022].

2.3.2 *Concentration of chromium(VI) in the primer coat according to the
product information*
To obtain information on the chromium(VI) content of corrosive-
resistant primers, an internet search was conducted to find safety data

sheets for relevant products. Safety data sheets were found for primers containing strontium chromate ($SrCrO_4$) and zinc potassium chromate ($Cr_2HKO_9Zn_2$).

The concentration of zinc potassium chromate in the primer coatings varied from 1 to 10%. A zinc chromate concentration of 7% was observed, while concentrations of zinc chromate hydroxide varied from 1 to 25%. The content given on the safety data sheet is nearly always a mass percent concentration. Unless otherwise indicated, the percentages in this report are also percentages by weight.

With regard to zinc chromate, the calculation of the chromium(VI) content in the dry layer of paint is partly based on the primer containing potassium **zinc chromate** ($KZnCrO_4$; Rust-Oleum) because the technical data sheet lists the physical properties of both the wet and dry paint for this product. *Altogether*, the calculation is based on, the five primers that have an average content of zinc chromate equivalent of 8 mass percent (% m/m) and an assumed concentration of solids of 60% (m/m). Based on these specifications, the chromium(VI) content has been calculated to be 4% (in round numbers), which is equal to 40,000 ppm, i.e. 40,000 mg/kg of dry paint. Based on the concentrations found in the safety data sheet the lower limit value is 1% and the maximum total **zinc chromate** content is 25% in the liquid paint. Using these limit values, the concentration of chromium(VI) in the dried paint can vary from 0.5–12.5%. This is equivalent to a concentration of 5,000–125,000 mg/kg (i.e. ppm) in the dry paint.

With regard to strontium chromate, the concentrations listed on the safety data sheets of the primers vary from 10 to a maximum of 42% m/m. Based on the data from the safety data sheets, an average content of 20% strontium chromate and a solid content of 50% were assumed when calculating the chromium(VI) content of the dry primer coat. On the basis of these numbers, the average chromium(VI) content in the dry primer is 10%. The text box below contains an explanation of the calculations. Assuming a lower limit of 10% and a maximum total **strontium chromate** content of 40% in the liquid dry paint, the concentration of chromium(VI) in the dry paint can vary from 5–20%. This is equivalent to a concentration of 50,000–200,000 mg/kg (ppm) in the dry paint.

Text box Calculating the chromium(VI) content of the dry primer coat:
Step 1: 20% strontium chromate in wet paint that contains 50% solids means that dry paint contains 40% strontium chromate.
Step 2: in strontium chromate, chromium accounts for 25% of the mass. This is derived from the atomic masses of the elements that comprise strontium chromate.
Step 3: the dry primer therefore contains 25% of 40% = 10% chromium(VI).

2.3.3 *Concentration of chromium(VI) in the total paint layer according to the product information*
The aforementioned concentrations apply to the primer layer. A primer layer is finished off with a top coat, with an optional extra intermediate layer as well. In order to compare the calculated concentrations with the measured values presented in sub-section 2.1.4, these intermediate and top coats must be taken into account. This is because when a sample is taken, it usually includes the entire paint layer. The calculations and results described in this sub-section are intended as a rough estimate of the content that one can expect to find in new paint layers. As previously stated, the number of layers applied and the thickness of the paint coats can, in practice, vary considerably.

With regard to the primers discussed above, the thickness of the dry paint layer for **strontium chromate** and **zinc chromate** has been assumed to be 30 and 40 μm (respectively), based on the product information found. How many layers are applied on top of the primer coat and the thickness of these layers depends on the conditions to which the painted object will be exposed and the durability of the coating [Sika, 2022]. The top layer is usually thinner than the intermediate layer. The sample calculation offers a breakdown for paint systems with a total of two and three layers, including the primer. The layers have an average thickness of 100 μm (in a system with a total of three layers, the intermediate layer is assumed to have a thickness of 120 and the top layer a thickness of 80 μm). The thicknesses specified here pertain to the dry layer of paint.

To calculate the chromium(VI) content of the total paint system, one must first know the density of the dry paint layers. For a number of paints, this density can be calculated using the technical specifications for the coatings in question. The density of the dry paint can be calculated in multiple ways (see Figure 2.1). For example, it can be done using the percentage of solids by volume and mass percent and the density of the liquid paint, but also based on the percentage of volatile components, the density of the wet paint and the percentage by volume of solid components. In both cases, in addition to the density of the wet paint, the volume percentage of solid substance (which can be calculated from the thickness of the wet and dry paint layers) is needed. When calculating the density based on the percentage of volatile components, it is assumed that any volatile components are no longer present in the dry paint layer. The remaining quantity of material constitutes the solid paint.
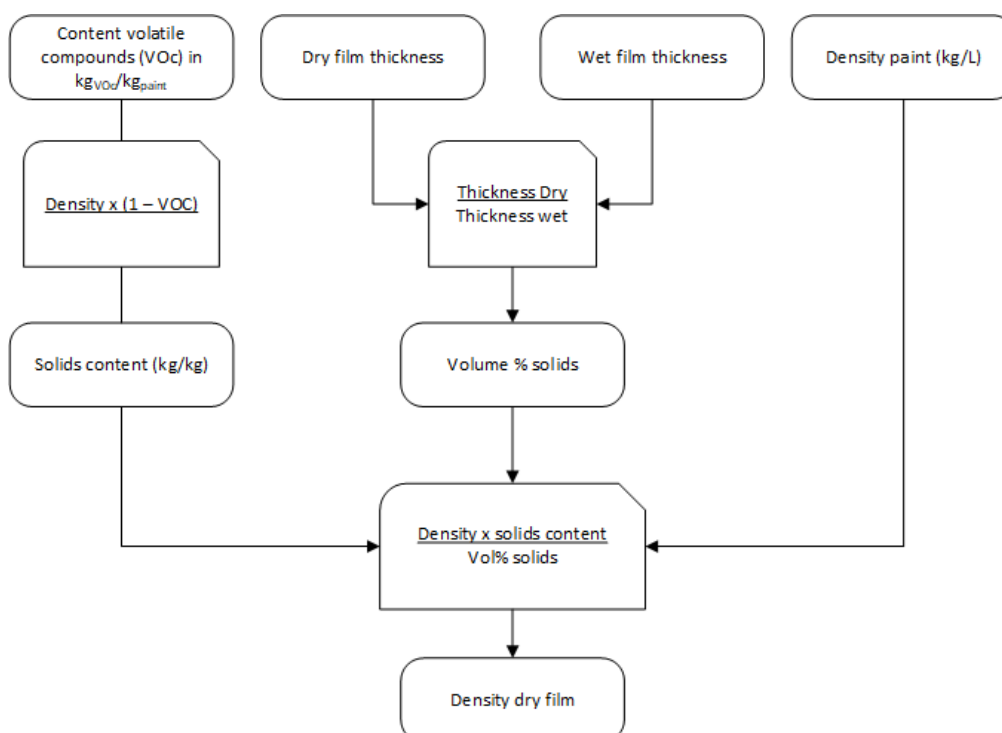
Figure 2.1 Flow chart for calculating the density of a dried paint layer

Based on analysis of twelve different coatings [PPG, 2022 and Sika, 2022], the average density of the dry paint was calculated to be 1.66 kg/L. For the two primers described above, the density of the dry layer of paint was 1.69 and 1.80 kg/L, respectively. Here we have assumed a single density of 1.7 kg/L for all layers of paint. If it is assumed that neither the intermediate layer nor the top coat contains any chromium(VI) and the sample taken includes all paint layers, then the average chromium(VI) content in the total paint layer in the case of a primer containing **strontium chromate** with a single top coat is 23,000 mg/kg and, in cases where there is both an intermediate layer and a top layer, 13,000 mg/kg. For a primer containing **zinc chromate**, the chromium(VI) content in case of a top coat alone is 11,000 mg/kg and for both an intermediate layer and a top coat, it is 7,000 mg/kg. See Table 2.1 for an overview of the results of the calculations. The calculated contents for the entire paint system are based on previously presented average contents in the primer layer. They can be calculated easily in proportion to the respective thicknesses of the layers because it is assumed that all paint layers will have the same density. The numbers show the average content across all removed paint layers. This is because the total paint layer is almost always removed when taking samples of old paint layers.

Table 2.1 Calculated chromium(VI) content across all paint layers of the object examined

Ingredient	Primer		Total paint system			
			1 top coat		Intermediate and top layer	
	Concen-tration (mg/kg)	Thickness of layer (µm)	Thickness of layer (µm)	Concen-tration (mg/kg)	Thickness of layer (µm)	Concen-tration (mg/kg)
Strontium chromate	100,000	30	130	23,000	230	13,000
Zinc chromate	40,000	40	140	11,000	240	7,000

These calculations show that the chromium(VI) content of the entire paint layer is lowered by a factor of 3 to a factor of 8, depending on how many additional layers are applied on top of the primer layer. In 2.3.4, the calculated concentrations are compared to the measured concentrations of chromium(VI) in old paint layers.

2.3.4   *Measured chromium(VI) concentrations in applied paint layers*
This sub-section addresses the results of investigations in which the chromium(VI) content of old paint on painted objects was determined. In the past 10 years, there has been growing attention for the possibly of workers being or having been exposed to chromium(VI) while carrying out repair work on painted objects and removing damaged layers of paint that contains chromium(VI). Numerous studies have been conducted on the presence of chromium(VI) in paint layers on rolling stock such as trams and train carriages, steel constructions such as locks and bridges and military equipment such as tanks and aircraft. Table 2.2 provides an overview of measurement results from a number of recent investigations at various companies. The study conducted by Van Rooij [2020] showed that, when old paint contains chromium(VI), the average concentration is between 1,000 to 3,000 mg/kg, with occasional outliers of up to 10,000 mg/kg. For details of the measurement results, see Table 2.2.

Table 2.2 Measured chromium(VI) concentrations in samples of paint from various companies. Data taken from [Van Rooij, 2020].

Company	No. of paint samples	No. of samples with Cr-VI		Cr-VI concentration in samples containing Cr-VI (mg/kg)		
	N	N	%	Average	Lowest	Highest
Company 1	19	15	79	1,040	200	3,000
Company 2	219	17	8	2,802	18	8,330
Company 3	34	19	56	2,167	40	9,780

With regard to this study, no other information is known about the companies where the samples were obtained or from what kind of objects the samples were taken. Neither is any information available about the sampling process, or whether portions of the paint layers were sampled or if each sample involved removing the entire paint layer down to the bare metal surface.

A study commissioned by Dura Vermeer and conducted by Antea Group [2019] into the presence of chromium(VI) on a sheet pile wall construction found that chromium(VI) was not present in the sampled paint layers at concentrations above the detection threshold of 10 mg/kg (ppm).

Another investigation looked at the presence of chromium(VI) and other heavy metals in paint layers on various components of trams [SGS, 2019]. Chromium(VI) was found in the paint samples taken from every investigated part, with the exception of the pantograph (i.e. the conductor between the overhead wire and the tram). The measurement data can be found in Table 2.3.

Table 2.3 Measured concentrations of chromium(VI) in paints on various tram parts (mg/kg).

Description of sample location	Concentration (mg/kg)	Paint colour		Surface material
		Primer	**Top coat**	
Mp2 bogie motor	250	-	Black	Steel
Mp4 shaft coupling	3,000	Green	Blue	Steel
Mp5 front left door of tram	200	Red	Yellow	Aluminium
Mp6 pantograph	<1.0	White	Black	Steel
Mp8 tram roof	1,300	Green	Black	Steel
Mp9 underside of tram carriage	390	-	Dark grey	Steel

The limit of detection for the applied analysis method is in keeping with EN 15192, having a detection limit of 1 mg/kg for chromium(VI). The SGS report states that a green primer layer was found on the various parts and that earlier studies had shown that this primer contains chromium(VI). The highest concentrations found were indeed measured on the parts with a green primer layer; see Table 2.3. A green colour would therefore seem to be an indicator that a primer contains chromium(VI).

Chromium(VI) concentrations can also be derived from a previous study into exposure to chromium(VI) that occurred while working with objects that had been treated with paint containing chromium(VI). That study was commissioned by the Stichting Arbeidsomstandigheden en Spoorwegveiligheid (SAS) [Peters, 2018] and focused on objects located alongside the rail network, including bridges, viaducts, tunnels, overhead portal structures, signal posts and lamp posts. This research showed that the measured exposure concentrations for released dust and the amount of chromium(VI) were highest when work involved a relatively large surface area of the protective coating (paint) and the paint layers were entirely removed. Such work includes sanding down to the bare metal with a grinding/deburring disc and sanding using an electric sander. This type of work was primarily carried out on locomotives and shunting engines. With regard to these two types of task, the chromium concentrations calculated for the collected dust are shown in Appendix A. Assuming that the dust collected consists largely of the pain that was removed, the measured concentrations are

representative for the concentrations in the paint present on the treated objects. The chromium(VI) content of this substance has been calculated to be between <385 and 3,149 ppm. The concentrations in the dust collected during sanding/grinding vary from 351 to 6,473 ppm. The Dutch Directorate-General for Infrastructure and Water Management (Rijkswaterstaat) has arranged various studies for measurements to be taken, in order to quantify the chromium present in the paint layers on a number of objects under its management [RPS, 2019a and b; NEBEST, 2021a, b and c]. Table 2.4 provides a summary of the measurement results.

Table 2.4 Measured concentration of chromium(VI) (mg/kg) on objects under management of Rijkswaterstaat

Object name	Limit of detection (mg/kg)	Number of samples	No. of samples with Cr-VI	Concentration (mg/kg)	
				Minimum	Maximum
Haringvliet bridge	20	79	20	200	6,204
Sambeek dam	20	20	9	1,819	7,999
Belveld dam	10	32	8	118	3,331
Oosterschelde flood barrier	10	43	16	18	1,530
Brienenoord bridge	10	163	31	22.1	7,030

The highest concentrations were measured on a limited number of parts of the structure, particularly on stair-rails and other railings and shipping signal posts. The colours orange, yellow and green generally contained the highest concentrations. Typically, the weight-bearing elements (such as the beams and the deck) and the main components (such as the dam valve) contained relatively low concentrations (about 20 mg/kg) or even no chromium(VI), with the exception of the eastern arch of the Brienenoord bridge. The weight-bearing elements of the Brienenoord bridge (arches, deck and beams) appear to have been coated with lead paint (lead content in the order of several hundred grams per kilogram of paint).

The case of the Lek bridge near Vianen demonstrates the necessity of taking measurements. Initially, the protective coat on the main weight-bearing structure of the bridge was presumed to contain red lead [Witteveen and Bos, 2017]. At a later stage, however, the scrap from the bridge was shown to contain chromium(VI) as well.

2.3.5 Conclusion with regard to chromium(VI) in paint layers

The results of the three studies conducted on old paint layers in the Netherlands provide a consistent picture, with comparable distribution and concentrations in the same order of magnitude. Concentrations of chromium(VI) in old paint layers appear to range from 20 ppm to a maximum of 10,000 ppm. On average, the concentration is around 2,000 ppm (0.2%) Although some details of the sampling process remain unknown, it can be assumed that these concentrations apply to the entire paint layer.

The calculated chromium(VI) content of the primer is approximately 40,000 ppm (4%) for zinc chromate and 100,000 ppm (10%) for strontium chromate. For a sound comparison with the measured data, the paint layers on top of the primer must be taken into account, which will in effect 'dilute' the concentration. When this is considered, the maximum measured concentrations (3,000 to 10,000 ppm) are reasonably similar to the calculated values (7,000–23,000 ppm). It is difficult to provide an average value considering the wide range of measured concentrations and the limited dataset. The average measured concentration seems to be somewhere around 2,000 ppm. The highest calculated concentrations are, however, above the maximum measured value. The calculated concentrations are based on the average chromium content in the two different types of primer, the actual spread in calculated concentrations being higher. The concentrations found in the primers, differ a factor of 7 for zinc chromate and a factor of 4 for strontium chromate. This increases the extent of the overlap with the dispersion present in the measurement data.

There could be a number of reasons why the average of the measured concentrations is lower by a factor of 3 to 10 compared to the calculated concentrations. One possible explanation is that, over time, a portion of the chromium(VI) in the primer has reacted and been *reduced to trivalent chromium* in the formation of the protective layer of Cr_2O_3 as a result of contact with oxygen and water [Gharbi et al., 2018]. All coating systems let through some moisture and air to some degree, meaning that over time, some degree of conversion of chromium(VI) will occur. The extent of this conversion depends on how strongly the coating system is affected by environmental factors such as moisture, grime, temperature and UV radiation, in combination with the lifespan and durability of the coating system [Scholten, 2021]. That being said, conversion is primarily associated with morphological defects in the coating, such as in the event of wear or damage to the coating, for instance as a result of mechanical stress [Gharbi et al., 2018].
It is also possible that during maintenance painting work, a portion of the original paint layers (including the primer) have been *removed and replaced with chromium(VI)-free coatings* or *that additional chromium(VI)-free paint layers* are applied on top of the existing intact layers resulting in a lower total chromium(VI) content as well.

In the next sub-section, the calculated chromium(VI) concentrations in the primers are used to give an idea of the chromium(VI) content one could expect to find on treated metal objects – in this case, recently-painted metal objects. With regard to scrap, the chromium(VI) concentrations – as revealed in the measurement results shown and for the aforementioned reasons – will be lower. In that sense, the chromium(VI) concentrations for steel objects treated with paint (which are based on the calculated concentrations in the paint) should be taken as a worst-case.

2.3.6   *The concentration of chromium(VI) from paint present in steel scrap*
This sub-section addresses in greater detail the amount of chromium(VI) present on painted steel. Several example calculations of the expected concentrations in scrap are provided. This provides a general picture of

the possible chromium(VI) content of scrap originating from coated objects.

In the previous section, we indicated that the paint on treated steel typically consists of a primer overlaid with a top coat. The protection against corrosion derives from the corrosion-resistant additives present in the primer. As previously indicated, the top coat may also contain pigments with chromium(VI) in them, though the measurement data contains no direct indications of this.

The example calculations assume that only the primer layer contains chromium(VI). Two scenarios have been elaborated, one for steel beams and one for sheet steel of two different thicknesses. Figure 2.2 is a flow chart showing how to calculate the amount of chromium(VI) present on sheet steel and construction beams. To calculate the quantity of chromium(VI), one must know the surface area to be painted per kg of steel. This depends strongly on the shape of the object being painted. The quantity of paint to be applied per square metre of surface area derives from the thickness of the layer(s) to be applied. The chromium(VI) content of the paint and the density of the wet paint are used to calculate the quantity of chromium(VI).
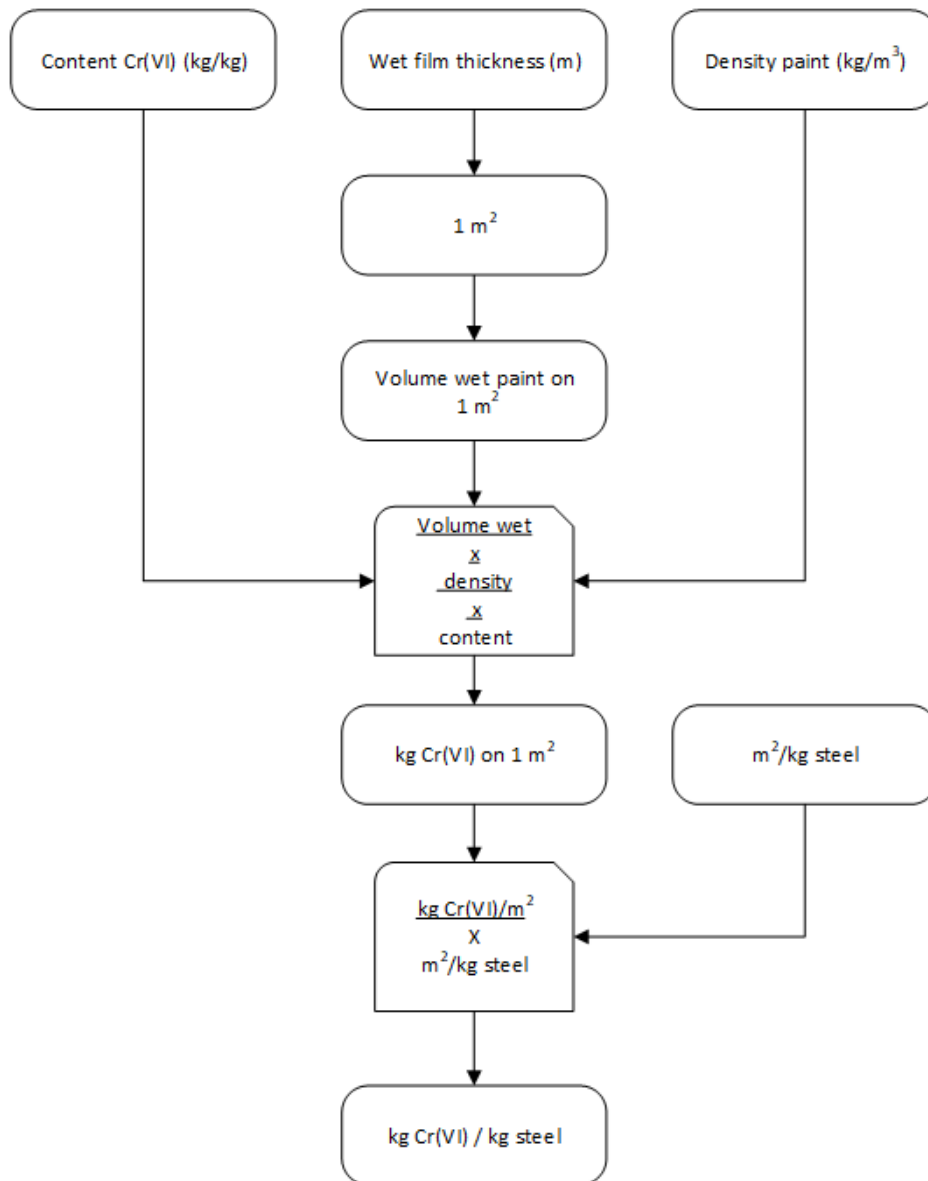
Figure 2.2 Flow chart for calculating the amount of chromium(VI) on painted steel (kg chromium(VI)/kg steel).

The first example is based on a steel beam with a length of 178 mm and a width of 102 mm (mass of 19 kg/m). The flange is 8 mm thick and the web is 5 mm thick; see Figure 2.3. For every metre of beam, the surface area in need of a protective coating is 0.759 m². For the corrosion-resistant primers discussed in sub-sections 2.1.2 and 2.1.3, with calculated chromium(VI) concentrations between 40,000 ppm and 100,000 ppm for zinc chromate and strontium chromate respectively, the chromium(VI) content has been calculated to be 110 to 207 milligrams per kilogram steel.
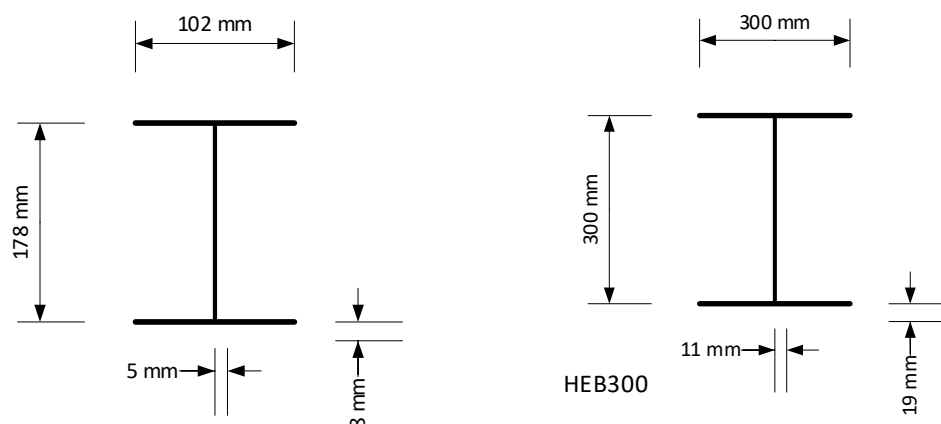
Figure 2.3 Dimensions of light (left) and medium-weight (HEB300; right) steel construction beams

For a medium-weight steel construction beam (type HEB300) as shown in Table 2.3, with a length and width of 300 mm (mass of 119.3 kg/m) and with flanges 19 mm thick and a web that is 11 mm thick, the chromium(VI) content will be 78 ppm for strontium chromate and 42 ppm for zinc chromate.

The second example involves painted sheet steel. Typical thicknesses for sheet steel used (among other applications) in the automotive industry are 0.7 mm for the vehicle body and 1.6 mm for the baseplate. With a steel density of 7.85 kg/L, the weight will be 5.5 kg/m^2 for a sheet with a thickness of 0.7 mm and 12.6 kg/m^2 for a sheet with a thickness of 1.6 mm. For comparison: in train carriages, sheet steel with a thickness of 0.8 to 2 mm is used for the exterior of the carriage body. Sheet-shaped elements used in construction are generally similar in terms of material thickness, varying from 0.5 to 1.75 mm [Gerrits, 2008, *Bouwen met staal* (Building with steel), 2007 and SAB, 2022].

Assuming the primers used are the same as those in the previous example, with layers of the same thickness, the chromium(VI) contents of (several kinds of) sheet steel have been calculated. These are shown in Table 2.5.

Table 2.5 Chromium(VI) concentrations for various thicknesses of painted sheet steel and two types of construction beams (ppm)

Type of material	Thickness of material (µm)	Concentration (ppm)	
		Strontium chromate	Zinc chromate
Body panel	700	942	501
Baseplate	1,600	411	218
Light beam		207	110
Medium beam		78	42

In the calculations for sheet steel, it has been assumed that only one side of the sheet has been painted with primer. It is reasonable to assume that only the exterior surface, which has the most exposure to

the elements, will be painted. That being said, it is impossible to exclude the possibility that, for certain applications such as baseplates, a corrosion-resistant protective layer has been applied to both sides. The average concentration from the ranges for the four types of material in Table 2.5 is about 300 ppm. The estimated average chromium(VI) content of 300 mg/kg is high considering the measured concentrations in paint layers on scrap (section 2.3.4), which are on average about a factor of seven (three to ten) lower than the calculated values.

2.3.7 *Conclusions regarding chromium(VI) found in paint in steel scrap*
The thickness and shape of the material from which the object is made clearly have a strong influence on the calculated chromium(VI) concentrations in painted steel. Sheet steel has a large surface area per unit of mass. For construction beams, the proportion is smaller and depends in part on the heaviness (i.e. the thickness) of the flange and the web piece. As a result, the quantity of chromium(VI) in painted sheet steel is considerably higher than in construction beams and in the case of thin sheet steel, it approaches 0.1 mass percent. In the event sheet steel has been treated on both sides with a rust-resistant primer, the concentration will exceed 0.1 mass percent.

2.4 Collection of steel scrap, specifications and quality standards

2.4.1 *Sources of chromium in steel*
Many different types and qualities (grades) of steel exist, with the characteristics and chemical composition of each having been laid down in standards. Section 3 addresses the different types of iron and steel in greater detail. The chemical composition greatly affects the mechanical characteristics of steel and therefore varies from one type of steel to another. The desired quality is achieved by adding alloying elements during the production process. At the end of the use phase, the different types of steel eventually end up in scrap and are therefore a source of chromium in discarded iron. The source of the scrap and the degree to which the different kinds of scrap are (or can be) sorted are factors which determine the chemical composition of the scrap. Table 2.6 provides an overview of the chromium content of various types of unalloyed and low-alloy steel. NEN-EN 10020:2000 sets out the definitions and categorisation of different types of steel. To help distinguish between unalloyed and alloyed types of steel, NEN-EN 10020 also contains limit values for specific elements. Unalloyed types of steel are types of steel that do not reach any of the limit values. The limit value for chromium is 0.3% [NEN, 2000]. For several types of steel, there is no limit value for the chromium content. If no specific limit value has been established, the limit value for the general type of steel to which a given product belongs will apply. Under EN 10025-2, for instance, no specific limit value for chromium has been established for hot-rolled structural steel. Because hot-rolled steel is classified as unalloyed steel [NEN, 2019], the applicable limit value for chromium is 0.3%. Unalloyed steel typically contains a maximum of 1.5% of alloying elements. Section 3 addresses the different types of iron and steel in greater detail.

Table 2.6 Chemical composition of various types of unalloyed and low-alloy steel, chromium content [MCB, 2022]

Type of steel	Cr content (%)	Remarks
Hot-rolled structural steel	-	EN 10025-2 compliant
LASER quality	-	
Thermomechanically rolled steel	-	EN 101149-2 compliant
Refined structural steel	Max. 1.5%	EN 10025-6 compliant
RAEX OPTIM QC	-	
Refined structural steel		
C45 and C60	≤0.4%	
25CrMo4 and 42CrMo4	0.90–1.20	EN 10083
Wear-resistant steel		
Boron-25	0.25–0.40	
X 120 Mn 12	≤1.5	
400HB	1.1	
Weather-resistant structural steel		
CorTen A	0.5–1.25	
CorTen B	0.50–0.65	
Heat-resistant structural steel		
P235GH–P355GH	≤0.3	
CrMo qualities	0.70–6.00	
Carbon steel		
16MnCr5	0.80–1.1	
20MnCr5	1.00–1.30	

Steel may also contain chromium without it having been intentionally added. This regards chromium that is present in the raw materials that are used in the production of steel (primarily iron ore and scrap). In an analysis of two samples of regular unalloyed steel, chromium concentrations of 0.342% and 0.016% were measured [Sengupta et al., 2011] (see also section 3).
Based on these measured concentrations and the chromium concentration in various types of steel presented above, the chromium content of regular unalloyed steel is expected to be below 0.3%.

2.4.2   *Quality standards and classification of steel scrap*
The European sector organisation for the recycling and recovery of iron, the European Ferrous Recovery and Recycling Branch (EFR), has established general quality standards and specifications for 11 different categories of steel scrap [EFR, 2007]. The Dutch sector organisation Metaal Recycling Federatie (MRF) is affiliated with the EFR. The specifications apply to unalloyed carbon steel, i.e. 'regular' steel, also known as structural steel. Scrap from unalloyed steel is used in processes such as primary steel production by means of the BOF process and in the production of secondary steel. Scrap from both unalloyed and

alloyed steel can be utilised for the production of alloyed steel. The specifications are typically compiled by sector organisations and may differ from one country to another. It is also possible that companies have specific requirements in place that have been agreed with the supplier.

The EFR has established as a general requirement that steel scrap may not contain hazardous materials, dirt and pollutants, and that, during the production of steel, it may not emit any substances that are harmful to health or the environment. This requirement does not specify what is meant by 'hazardous materials' or 'pollutants'. General requirements have also been formulated regarding the presence of other metals. With regard to chromium, all categories of scrap must be free from steel alloys and stainless steel (Inox), as well as free from mechanical components such as engines or motors, gear boxes, cogs, axles and tools. Scrap is also required to be virtually free of flammable materials such as rubber, plastic, wood and lubricants. Requirements regarding the presence of other metals have been formulated for each category of scrap. These requirements are typically met through application of the standard processing (sorting) methods and equipment used for scrap in the EU [EFR, 2007]. Here, too, no further information is provided as to what those standard processing methods and equipment should be. According to the stated requirements, the concentration of chromium should be less than or equal to 1% in swarf (borings, shavings, turnings, cuttings) that is formed by drilling into or shaving steel. The same applies to the residual category of steel scrap (high residual scrap). For old scrap, the concentration must be lower than or equal to 0.250% (sum total of chromium, nickel and molybdenum) [EFR, 2007]. In the descriptions for three categories of scrap, it is also indicated that these may not contain top coats (paint) unless otherwise agreed.

In the US, the Institute of Scrap Recycling Industries, Inc. (ISRI) has established guidelines for steel scrap which include a number of general specifications concerning the composition of the scrap. The guideline states that steel scrap is considered to be free of alloys if the residual chromium content (chromium that is present as an impurity) does not exceed 0.2% [ISRI, 2021].

2.4.3   *Literature review regarding the concentration of chromium in steel scrap*
A Swedish study [Willman et al., 2017] analysed the concentration of alloying metals in 88 samples of purified and shredded E40 scrap. E40 scrap consists of scrap from large household appliances, vehicles and household scrap that is obtained following the disassembly, shredding and sorting of the material, for instance through electromagnetic sorting and manual sorting. The scrap is sorted by hand to remove any high-alloy steel and copper. The highest chromium content in the samples analysed was 0.34%. In 14 of the samples, the chromium content was under the limit of detection (0.01%). The average chromium content of all samples was **0.032%.** Two samples had a chromium content which exceeded the ISRI specification of 0.2%. The EFR has not established a limit value for the chromium content of E40 scrap.

The concentration of impurities in steel scrap used in the production of steel rebar was analysed in an international study [Panasiuk et al.,

2022]. The researchers in this study opted to focus on reinforcing steel because of the high tolerance for copper content and because it has a higher concentration of impurities than other steel products. Table 2.7 displays the statistical data for the 179 samples for both scrap (n=65) and reinforcing steel (n=114). The highest concentration measured slightly exceeds the ERF standard of 0.25%.

Table 2.7 Chromium content found in scrap and reinforcing steel (%). General data from Panasiuk et al. [2022].

Chromium content (%)	
Minimum	0.02
Maximum	0.26
Average	0.12
5th percentile	0.03
95th percentile	0.21
Number of samples	179

The article by Tan et al. [2021] includes an overview of the concentrations of alloying elements in different types of steel scrap. Table 2.8 is based on specifications for steel scrap drafted by sector organisations (EFR and EUROSTEEL), businesses and (in a few cases) measurements. It is more an overview of the specifications than a report on the actual composition (though the specifications are based on actual measurements). The figures based on the specifications are therefore expected to yield an accurate picture of the concentrations that can be reasonably predicted for specific types of scrap.

Table 2.8 Chromium content (%) in various types of steel scrap in Denmark [Tan et al., 2021]

CN code	Explanation of CN code	Cr content (%)
72041000	Waste and scrap of cast iron (excl. radioactive)	-
72042110	Waste and scrap of stainless steel, containing by weight >= 8% nickel	11.5–18
72042190	Waste and scrap of stainless steel	
72042900	Waste and scrap of alloy steel	0.4–10
72043000	Waste and scrap of tinned iron or steel	-
72044110	Turnings, shavings, chips, milling waste, sawdust and filings of iron or steel, whether or not in bundles	0–0.75
72044191	Trimmings and stampings of iron or steel, in bundles	-
72044199	Trimmings and stampings of iron or steel, not in bundles	-
72044910	Waste and scrap of iron or steel, fragmented ('shredded')	0.14–0.2
72044990	Waste and scrap of iron or steel, not fragmented ('shredded'), not in bundles	0–0.195

In the data collected by Tan et al. [2021], a distinction should be made between alloyed steel (72042110, 72042190 and 72042900) and unalloyed (carbon) steel, which includes the remaining types of steel

scrap (except for 72043000, which comprises tin-coated cans). While the steel alloys and tin-coated steel are not used in the production of regular steel, they are used in the production of steel alloys. According to Tan et al. [2021], the chromium content of scrap that can be utilised in the production of steel varies from 0 to 0.75%; see Table 2.8. The study by Kato and Ono [2021] assumes that the average chromium content of scrap is 0.175%. In their article, Mousa et al. [2022] mention scrap with a chromium content of 0.06%.

2.4.4   *Conclusion regarding the quantity of chromium in steel scrap*
The quality specifications do not provide a limit value for the chromium(VI) content in the various categories of steel scrap. The limit values apply solely to the total chromium content. In the studies consulted, only the total chromium content was reported. The literature review that was conducted yielded no information on the presence of chromium(VI) in scrap.

According to the specifications for steel scrap drafted by the European sector organisations, the total chromium content of old (unalloyed) scrap may not exceed 0.25%, while the American guidelines require a value of 0.20% or lower in order to be considered unalloyed steel scrap. According to the European standard, the chromium content in new scrap – i.e. scrap resulting from metalworking processes – must be less than or equal to 1%. Tan et al. [2021] reported a value of 0.75% for this. The maximum chromium content measured in shredded scrap in Sweden was 0.34%, with an average of 0.032%. The other two studies recorded concentrations in between this average and the maximum. The average chromium content of scrap used in the production of reinforcing steel was 0.12% and the amount of chromium in chrome-plated tin used as a packaging material was between 0.007 and 0.022% (see Table 2.9).

Table 2.9 Total chromium content of various types of scrap

Type of scrap	Content (%)		Type of value	Source
	Min.–max.	Average		
Unalloyed old scrap		0.20; 0.25	Limit value	[ISRI, 2021]; ERF [2007]
New scrap		1%; 0.75	Limit value	ERF [2007] ; Tan et al. [2021]
Scrap for reinforcing steel	0.02–0.26	0.12	Measured	Panasiuk et al. [2022]
Cleanly shredded	<0.01–0.34	0.032	Measured	Willman et al. [2017]

We see that relatively impure scrap that is used to produce reinforcing steel is virtually always within the limit value set by the ISRI. Relatively clean and well-sorted scrap complies with the limit values as well, with perhaps a handful of exceptions. On average, the concentration found in the latter type of scrap can be expected to be lower than that of scrap that is used in the production of reinforcing steel. Chrome-plated tin

generally contains a smaller quantity of chromium with a maximum concentration that is below the average of well-sorted scrap.

Scrap from unalloyed steel can be assumed to have an average concentration roughly equal to 0.1%. Based on a study conducted in Sweden, effectively-sorted old scrap can be expected to contain lower concentrations of around 0.05%. In practice, the specifications for scrap will usually be met because the specifications for the various types of scrap are based on actual data.

2.5 Share of steel scrap that contains chromium(VI)

This sub-section addresses the quantity of steel scrap iron that is processed by the iron industry in the Netherlands for the purpose of making new steel. In addition, we give a rough indication as to the quantity of steel scrap containing chromium(VI) and what portion this represents of the total quantity of steel scrap processed in the Netherlands.

In 2016, the Dutch metal industry utilised around 1.8 Mton (1 megaton = 1 million tons) of ferrous scrap per year as a raw material for the production of new steel and steel alloys [Van Driel, 2019]. This quantity *includes* production scrap (part of which is scrap from the plant's own production process, that is reused in the production of steel, so called circulation or internal scrap). The remaining portion of the production scrap is marketed by scrap dealers.

Smitheries and foundries account for a small portion of the use of ferrous scrap, with a total processing capacity of 0.10–0.15 Mton. Production at these smitheries and foundries is based almost entirely on the use of scrap as raw material. The limited processing capacity of the smitheries and foundries in the Netherlands reveals that the majority of the ferrous (steel) scrap is utilised by the sole remaining customer who uses steel scrap as a raw material in the production of (primary steel): the Tata Steel plant in Velsen-Noord. This is also evident when we look at the quantity of steel scrap which Tata Steel uses for the production of steel.

Approximately 190 kg of steel scrap is needed to produce 1 ton of steel [EIB, 2012]. According to Corus (2006), 59 kg scrap is loaded into a steel converter along with 290 kg of liquid (crude) iron ; resulting in a share of 17% scrap and 83% liquid iron. These quantities will yield 325 kg of steel, resulting in a somewhat lower quantity of around 181 kg of scrap per ton of steel. In 2016, the total quantity of steel scrap needed for the total production of 6.9 Mton primary steel in the Netherlands assuming 190 kg of scrap per ton of steel is, 6.9 Mton x 0.19 ton/ton = 1.31 Mton scrap. This is somewhat less than the total quantity of ferrous scrap iron used by the Dutch metal industry, minus the quantity used by smitheries and foundries, 1.65 Mton.

The amount of steel scrap needed by Tata Steel consists partly of internally produced circulation scrap and partly of external scrap. The percentage of circulation scrap is around 10% of the production volume [Corus, 2006, Overduin and Ozinga, 2001 and RIZA, 1996]. The total

quantity of external scrap needed for the production of 7 Mton of steel is then around 0.6 Mton external scrap (1.31 – [10% x 7 Mton] = 0.6 Mton).

In the Netherlands, there are no numbers available on the quantity of collected steel scrap containing chromium(VI). Scrap that contains chromium(VI) must be labelled as such when it is sent to the scrap processor. However, no registration procedure exists for keeping track of how much scrap becomes available and where it goes. When scrap contains chromium(VI), there is a duty to inform (notification obligation) when transported to other countries, regardless of the percentage by weight [IenW, 2022]. The Human Environment and Transport Inspectorate (ILT) recently clarified this point on its website [ILT, 2023]. Information requested from the ILT shows that no notifications for scrap containing chromium(VI) have been requested since 2015 [FD, 2022b]. In practice, the origin and initial flow of scrap is difficult to trace. To gain a better picture of the composition of the scrap metal being exported, the national supervisory authority is working on an action plan in response to this issue [IenW, 2022].

Tata Steel in Velsen-Noord says that, in principle, it avoids using painted or galvanised steel so that it can reuse the oxygas dust in its steel production process [Corus, 2006]. Figures from Statistics Netherlands (CBS) show that the majority of ferrous scrap from the Netherlands is exported [CBS, 2023 and Van Driel, 2019]. According to Van Driel [2019], most inland recycling (reuse by smitheries and foundries) involves imported high-quality steel scrap from other countries and the scrap generated by the Dutch economy tends to be exported. The available statistics do not give exact quantities for either the imported scrap or domestic scrap reused in the Netherlands [CBS, 2023 and Van Driel, 2019].

To give an idea of the quantity of steel scrap that is suspected to contain chromium(VI), becomes available in the Netherlands, and the percentage of scrap that does contain chromium(VI), several examples will be provided to show the quantity of this kind of scrap that results from the processing of end-of-life infrastructure works, structures, means of transportation and heavy equipment.

ProRail [ProRail, 2023][3] and TenneT transported metal waste that potentially contains chromium(VI) to Purified Metal Company (PMC)[4]. In 18 months' time, PMC melted down 3,000 tons of this type of steel scrap [FD, 2022a]. In the Netherlands, TenneT has begun replacing a number of its high-voltage connections – specifically, removing the existing lattice towers and replacing them with so-called 'wintrack' masts. Existing lattice towers are usually constructed from galvanised steel. However, in order to extend the life time they are preserved by applying coatings about every 20 years [Hoogspanningsnet, 2023]. These

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[3] Since March 2021, ProRail has been turning its steel scrap containing chromium(VI) over to Purified Metal Company for safe, sustainable processing. Due to the use of paint containing chromium(VI) in the past, all painted steel objects belonging to ProRail may potentially contain chromium(VI) and must therefore be handled and disposed of as though they contain chromium(VI) [ProRail, 2023].
[4] Since the end of 2022 PMC was declared bankrupt, however, in the mean time the company is taken over and will probably continue to recycle contaminated steel scrap by the end of 2024 [IndustryLinqs, 2024].

coatings might contain lead and chromium (VI) [Tritium Advies, 2019]. A few figures are provided to give an idea of the amount of steel scrap that becomes available when old connections are refurbished or replaced. Between Vierverlaten and Eemshaven, for example, the relevant stretch has a total length of 50 km and 163 lattice towers which are being replaced. There are different types of lattice towers varying in configuration and size depending amongst others on the voltage level of the transport lines. It is assumed that each high-voltage lattice type transmission tower (pylon) weighs approximately 40 tons (Erp, 2021). This weight most likely relates to the larger sized lattice towers. The weight of smaller sized towers is in the range of about 10 tons (Börger, 2021 and 2013). That means that this project will result in 6,500 tons of steel scrap in the long term (i.e. after 2023). In 2019, 28 high-voltage pylons were removed between Moerkapelle and Leiderdorp. These pylons have a total weight of 1,100 tons (assuming 40 tons per pylon). The 110 high-voltage pylons between Tilburg-Noord and Best will be removed in 2027 at the earliest (yielding around 4,400 tons). Based on these numbers (together equalling 12 kilotons), the expectation is that several kilotons of this material will become available each year.

Jansen Recycling Group (JRG) has stated that its dismantling and processing of the old Botlek bridge yielded around 6,000 tons of steel scrap [JRG, 2022]. Also mentioned are two container cranes weighing 750 tons each and nine so-called straddle carriers (70 tons each) processed by the company. The total, then, is over 8,100 tons of scrap that is highly likely to include coatings containing chromium(VI). Jansen processes around 400 kilotons of scrap each year [Jansen, 2023]. If, for the purposes of a rough initial estimate, it is assumed that this is the quantity processed by the company in one year's time, this would indicate a total percentage of chromium(VI) containing steel scrap of somewhere in the order of 2%. Based on this percentage and the total amount of steel scrap processed[5] in the Netherlands in 2020 (5,882 kilotons), the quantity of scrap potentially contaminated with chromium(VI) could be in the order of 120 kilotons.

That being said, a few caveats are in order here. The measurement data for bridges and locks described in sub-section 2.3.4 reveals that, for some objects, only a limited number of their constituent parts will have been treated with paint containing chromium(VI). With regard to the Lek bridge, on the other hand, the weight-bearing structure had been treated with paint containing chromium(VI). It is evident from this data that it is extremely difficult to arrive at even a somewhat-accurate estimate of the quantity of contaminated steel scrap produced each year in the Netherlands. In addition, it is relevant to know whether the estimated percentage is representative for all steel scrap processing companies. There can be major differences between the type of waste processed into scrap by one company and the next. The companies in question may be specialised in processing large structures such as bridges and ships an in dismantling heavy equipment and machinery. There are also companies that focus mainly on processing end-of-life vehicles, electronics or construction waste into scrap. For this reason,

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[5] Quantity of ferrous scrap produced by the Dutch economy plus the quantity imported

the percentage of scrap that contains chromium(VI) will most likely not be the same for different processors of ferrous waste.

The next important question is how much of the ferrous scrap that becomes available in the Netherlands actually is processed by Dutch smitheries and foundries? This actually depends on the quantity and quality of the imported scrap and the exported scrap. Van Driel [2019] states that the relatively clean scrap is imported and processed, which would seem to suggest that scrap of a lower quality is – for the most part – exported. The fact that collect steel scrap is export for the greater part also has to do with the relatively limited processing capacity of the smitheries and foundries in the Netherlands in relation to the total quantity of scrap produced by the Dutch economy and the amount of imported scrap. An estimate of 2% of steel being contaminated with chromium(VI) therefore seems to be a on the high side considering the steel quality being processed by smitheries and foundries in the Netherlands. Therefore we assume an uncertain level of 1% of steel being contaminated with chromium(VI) in the further calculations.

Based on the percentage of 1% and an average total chromium content in steel scrap of 0.1% (section 2.4.4.) and a chromium(VI) concentration of 0.03% (300 ppm) in coated steel (see section 2.3.6), and assuming that the entirety of the potentially contaminated scrap has actually been treated with coating containing chromium(VI), then chromium(VI) would account for 0.3% of the total quantity of chromium in scrap (= the amount of chromium(VI) in scrap (1% x 0.3%) divided by the total quantity of chromium in steel scrap (0.1%)). These figures should be taken as an indication only (for the aforementioned reasons).

2.6 Conclusions regarding chromium(VI) in paint and steel scrap

For sheet material, the concentrations of chromium(VI) based on the mass of the steel product resulting from newly applied paint, are in the region of 0.02 to 0.09%. In light and medium-weight construction beams, the estimated concentrations are between 0.008% and 0.02% Considering newly applied paint, the concentrations for steel treated with chromium(VI) paints are in the same order of magnitude as the content of total chromium in well-sorted unalloyed steel scrap (0,05%) and approximately a factor of 10 lower than the concentration specified in the guidelines for scrap (0.25%). The latter is an accepted value based on actual scrap-processing practice. Due to a lack of information, it is difficult to draw conclusions as to what share of the total chromium in scrap is accounted for by coatings. To gain a better picture of this, an effective system for reporting and registration is required. It will also be necessary to consider practical measures to ensure contaminated scrap flows are kept separate and to avoid mixing them with clean scrap.

An first indication has been given as to what percentage of the total quantity of scrap processed in the Netherlands might contain chromium(VI). This number could be in the order of several percent. The chromium present in scrap can result not only from paint, but from other sources as well: chromium in the steel itself, chromium as a protective metallic layer or chromium in contaminated scrap (with steel alloys). Such contamination can be the result of incomplete dismantling

and sorting during the recycling of objects such as household appliances and cars. In addition, there are many types of steel that are potentially difficult or impossible to separate properly. The amount of chromium present in newly produced steel as a result of the production process is addressed in the following section. This section provides answers to research questions 1 and 4.

1. *What are the measured or expected concentrations of chromium(VI) in the paint layers on steel?*
   In the past – up until the late 1980s and early 1990s – chromium(VI) was added to rust-resistant primers. Most of the time, it concerned strontium chromate and zinc chromate. Lead chromate and barium chromate were sometimes used as well. Chromium(VI) has also been used as a pigment in top coats, especially for the colours red and yellow.

   Measurements conducted on old paint layers from bridges, locks and tram carriages show that chromium(VI) can be present. The concentrations may vary widely from one part of the structure being investigated to another. In some instances, only small parts may contain paint with chromium(VI) in it, while in others it covers the bulk of the object, such as the weight-bearing structure. Concentrations of chromium(VI) measured in chromium(VI) containing paints average around 1,000 to 3,000 mg per kg of dry paint, with a range of 20 mg per kilogram up to a maximum of 10,000 mg per kg of paint.

   Based on the safety and technical data sheets for chromium(VI) containing primers, the concentrations of chromium(VI) in both the primer layer and the total paint layer (including top coats) have been calculated. The calculated concentrations in the primer are in the range of 40,000 mg per kg of dry paint for zinc chromate and around 100,000 mg per kg of dry paint for strontium chromate. For the entire paint layer, the concentrations range from 7,000 to 20,000 mg per kg of paint. This is higher than what the measurements show. The higher calculated concentrations can for instance be explained by the fact that during the lifespan of the painted object, part of the chromium(VI) is reduced to trivalent chromium due to external influences such as moisture, or that a portion of the paint has been removed in the course of maintenance. It is also possible that during maintenance painting work, a portion of the original paint layers (including the primer) has been removed and replaced with chromium(VI)-free coatings or that additional chromium(VI)-free paint layers are applied on top of the existing intact layers resulting in a lower total chromium(VI) content as well.

4. *What quantity of chromium (total and chromium(VI) specifically) is present in steel scrap in the following component:*
   a. *Paint layers containing chromium(VI)*
   b. *The bulk of the steel scrap*

Based on the calculated concentrations of chromium(VI) in the primer, the chromium(VI) content of the painted steel objects has been calculated. These calculations have been carried out for various thicknesses of sheet steel and for two types of steel construction beams. With regard to thin sheet steel, the highest concentrations approach 0.1% and the average lies around 0.05% (Table 2.5), if the paint is assumed to be on one side only. Heavier materials such as construction beams tend to have lower concentrations, in the region of 0.008%. Based on the calculations, the average for newly painted steel is around 0.03% (300 ppm).

No measurement or other data was found on chromium(VI) concentrations in scrap. However, data is available on the total chromium content of scrap. According to the quality standards for scrap established by European sector organisations, unalloyed steel scrap contains a maximum of 0.2% chromium. Based on measurement data, scrap from unalloyed steel can be assumed to have an average concentration roughly equal to 0.1%. Well-sorted old scrap is expected to have a chromium content of around 0.05%.

The quantity of scrap containing chromium(VI) that is generated in the Netherlands is unknown. A rough estimate has been made as to what percentage of the total quantity of scrap generated in the Netherlands could potentially contain chromium(VI). The percentage may be in the region of (up to) several percent. The expectation is that only a limited portion of the scrap generated in the Netherlands will be processed by Dutch smitheries and foundries. A considerable portion of the scrap processed by these facilities in the Netherlands is 'clean' circulation scrap. The smitheries and foundries also appear to use primarily 'clean' scrap imported from abroad. Consequently, the waste scrap or scrap from end-of-life products that becomes available in the Netherlands will, to a large extent, be exported to other countries. When considering the use of contaminated steel scrap in the Netherlands, an uncertain estimate is 1% of the steel scrap being contaminated with chromium(VI). This could be on the high side due the fact that steel scrap collected in the Netherlands is largely exported and relatively clean scrap is imported and internal scrap is processed by foundries in the Netherlands.

3 Sources of chromium in steel production

3.1 Introduction

In this section, we first provide a brief explanation of the different types of iron and steel and the different production processes for producing primary or new steel and for producing steel from steel scrap, i.e. secondary steel. After that, we discuss the various production processes in greater detail. The sub-processes and raw materials used in the production process are addressed. Based on the chromium concentration of the raw materials, we have drawn up a balance for each of the various sub-processes and for the different processes as a whole. In doing so, we have estimated how much chromium enters the process and how much ends up in the final product. Where information on chromium(VI) has been found, this is explicitly mentioned. The available information pertains virtually exclusively to the total quantity of chromium. We also provide an overview of the emissions of chromium during production and the amount of chromium present in the by-products and waste flows resulting from the process. Lastly, we conduct an analysis of the emissions generated by the different production processes for steel production. Based on this analysis, we make an estimate as to what happens to the chromium(VI) in the coatings (paint) during the stage of the production process in which scrap it utilised. The critical process steps and process conditions are distinguished and elaborated as well.

This section addresses the following research questions:

2. What are the emissions of chromium(VI) (and potentially other relevant metals) into the air (and, where possible, those into water and in waste flows) from various types of steel plants (per ton of produced steel)?
3. What is the range for quantities of chromium in the primary raw materials of steel (per ton of produced steel)?
5. Where does the chromium from these sources end up? (flue gas treatment residues, emitted fine and other particulate matter, waste/drainage water, alloying with newly produced steel, and so on)

3.2 Types of iron and steel

The iron and steel that are produced and placed on the market are actually alloys of iron and carbon. Steel has a carbon content varying from around 0.05 to 2.1 percent depending on the steel grade. A material with a higher carbon content is cast iron, which can have a carbon content of up to 4.5%. Besides carbon, other elements such as chromium, nickel, vanadium and tungsten are often added in order to enhance certain qualities, for instance flexibility, tensile strength and rust-resistance.

'Carbon steel' is a commonly used term that indicates (as explained above) that the material in question is actually an alloy of iron and carbon. Carbon steel can refer to both steel and steel alloys. Often, the term carbon steel is used to refer to types of steel other than high-alloy steel, such as stainless steel [Callister, 2007]. In other words: the terms

steel and carbon steel frequently refer to the same thing, namely 'regular' unalloyed steel. For carbon steel, maximum concentrations are often established for the elements manganese (1.65%) and silicon (0.6%) as well.

Depending on the carbon content and the classification system, three main categories of carbon steel are distinguished – low, medium and high – which can be further broken down into sub-categories [Callister, 2007]. According to the system applied by the American Iron and Steel Institute (AISI) and SAE International (Society of Automotive Engineers), steel can be divided into four main categories based on its carbon concentration [Total Materia, 2001 and Carbon steel, 2022]:

- Low-carbon steel (0.05–0.15%)
- Medium-carbon steel (0.3–0.5%)
- High-carbon steel (0.6–1.0%)
- Ultra-high-carbon steel (1.25–2.0%)

With regard to the concentration of alloying elements, a further distinction is made between unalloyed steel that contains a maximum of 1.5% of alloying elements (excluding carbon); low-alloy steel that may contain a maximum of 10% of alloying elements; and high-alloy steel in which the concentration is 11% or more. The latter category includes stainless steel, also known as Inox steel. Stainless steel contains a minimum of 11–12% chromium and a maximum of 1.2% carbon [Steel, 2022; Stainless steel, 2022]. Other percentages are used to categorise certain types of steel as well: up to 1.5% for unalloyed steel, 1.5–5% for low-alloy and concentrations higher than 5% for high-alloy steel [Tosec, 2022 and Metaal Nederland, 2022]. Stainless steel also contains nickel. The most common type of stainless steel is type 304, which has a chromium content of 18% and a nickel content between 8 and 10% [Stainless steel, 2022].

Alloying elements may also be added to non-steel types of iron such as cast iron to alter the characteristics of the metal. Besides carbon, silicon is the most important alloying element in cast iron, which has a silicon content of 1 to 3%. The manganese content is no more than 1%. Nickel is one of the elements most commonly added to cast iron to increase durability. Chromium may also be added in small quantities (around 0.5%) [Cast iron, 2022]. It is possible to distinguish between various types of cast iron, including grey, malleable, ductile and white cast iron. White heart (GJMW) and black heart (GJMB) are two types of malleable cast iron [Vanotools, 2006].

The preceding makes it clear that great variety exists among the different types of steel and iron. The most relevant, main steel categories are:

- Low-alloy steel such as regular steel (also known as carbon steel)
- High-alloy steel such as stainless steel

In this report, a distinction will be made (where necessary) between the production flows for these two categories of steel. This is particularly important with regard to the emissions and the chromium content of the by-products being formed. This section, however, focuses on the production of unalloyed steel.

3.3 Iron and steel production processes

With regard to unalloyed steel production, a distinction can be made between primary steel production and the production of secondary steel. The production of steel can be divided into four main processes, see Figure 3.1.

Primary steel is made from iron ore. In blast furnaces the iron ore is converted to crude iron, . In the next step, crude iron is combined with scrap in the steel plant to produce steel. When the production of crude iron and steel take place at the same location, the site is referred to as an integrated steel plant. In integrated steel plants the crude iron is transferred in the liquid state and therefore also referred to as liquid iron or hot metal. Less common is when a blast furnace and a steel plant operate independently. In that case, the crude iron is usually delivered in the form of ingots (this is where the term pig iron stems from) to the steel plant at a different production location. Only two such plants exist in the EU. In addition to the blast furnace process, there are also two alternative methods that are similarly based on the reduction of iron ore:

- The Corex/Finex process. In this process (not using sinter), the primary reduction of iron ore (using coal instead of coke) is followed by smelting and then conversion of the iron smelt into steel by means of the BOF process. This process is not used in Europe.
- The DRI process. Direct reduction of iron ore, followed by conversion into steel using an electric arc furnace. Currently there is only one DRI plant in operation in Europe (AcelorMittal, Hamburg).
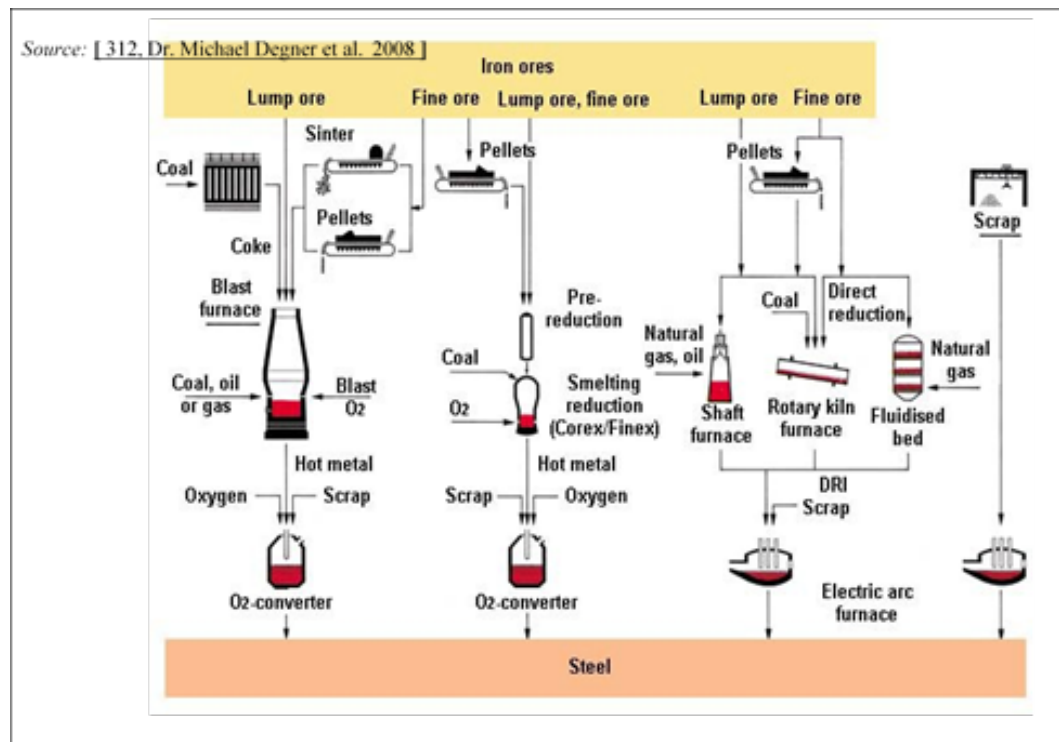
Figure 3.1 Overview of the four steel production methods: the first process is based on the blast furnace in combination with the oxygen steel converter, the second is the production of iron melt according to the Corex/Finex process in combination with the oxygen steel process. The third process is the direct reduction of iron combined with the production of steel in electric arc furnaces. The last process is entirely based on the production of steel from steel scrap in electric arc furnaces.

We can distinguish secondary steel production as a fourth process. Secondary steel is produced primarily from scrap. This is typically done in electric arc furnaces, generally referred to by the acronym EAF. This acronym will be used in this report as well. Besides electric arc furnaces, induction furnaces can also be used in steel production. Induction furnaces are primarily employed by foundries. Foundries use iron pigs, steel scrap and foundry returns as raw materials. In the Netherlands, there is a dedicated plant with a capacity of 150 kilotons per year where steel scrap is melted down in induction furnaces and where contaminant on the scrap (such as asbestos) are removed during the melting. The resulting product (pigs) are then sold to be utilised in the production of cast iron, steel and steel alloys [Recycling International, 2021]. Stainless steel and other steel alloys are generally made from (stainless-) steel scrap and other alloyed scrap with the help of electric arc furnaces. After smelting, the carbon present in the metal is extracted by means of the argon-oxygen decarburisation (AOD) process. During this process, alloying elements are also added to achieve the desired composition. Removing carbon and altering the composition may be carried out in the EAFs as well, either wholly or in part. After that, fine-tuning often takes place in a separate furnace, usually a ladle furnace.

3.4 Integrated steel production, primary steel

Primary steel can be produced from iron ore in a variety of ways as mentioned previously. The most common method is the process which uses blast furnaces to turn iron ore into molten iron. After that, the hot metal is combined with steel scrap in the oxygen converter, where – by means of the conversion process – steel is produced. In the conversion process, pure oxygen is blown into the molten iron so that it can react with the carbon present in the hot metal feed. This takes place inside what is known as a converter. The converter is a concave furnace with a heatproof lining into which the hot metal is transferred. Another name for this converter is the basic oxygen furnace (BOF). While the oxygen is being blown in, carbon monoxide and carbon dioxide are formed. In this way, the carbon content is reduced to the desired level. Other substances form while the oxygen is being blown in as well, namely oxides of other metallic elements that are present and of silicon. These oxides combine with the introduced slag forming agent – mainly limestone ($CaCO_3$) and burnt lime (CaO) – to form liquid slag which floats on top of the molten iron. The slag must be separated from the molten steel before the steel can be further refined.

This sub-section offers an overview of the quantity of chromium that may end up in the produced steel through the raw materials. All raw materials used contain some chromium, though this amount varies. The chromium contents of the different raw materials have been identified by means of an extensive literature review. The amount of chromium that can potentially be present in scrap was discussed in the preceding section. A summary of the data on chromium concentrations in the raw materials is included in Appendix B. The information is displayed per raw material. Appendix B also includes the mass balance for chromium in all sub-processes, e.g. the production of coke, sinter, pellets, crude steel and steel. This was done simply by multiplying the quantity of each raw material used by the chromium content of that material. Also taken into account was the loss of chromium, for instance due to its partial absorption by the slag or emission into the air. In this way, the chromium content of every intermediate product was estimated. Finally, we used the chromium contents of the intermediate products to calculate the chromium content of the final product, i.e. the steel. The use of raw materials and the formation of by-products during the use of electric arc furnaces are addressed in the section on secondary steel production.

3.4.1 Production process and usage of raw materials in steel production

In addition to iron ore and scrap, the production of steel also requires various kinds of raw materials and additives. A diagram of the integrated steel production process and the necessary raw materials is shown in *Figure 3.2*. In an integrated steel plant, the iron oxide in the ore is reduced in the blast furnaces with the help of a substance called 'coke'. Furnaces known as coke ovens are used to turn coal into coke. In the process, a fine coke fraction (coke breeze) is formed. Iron ore is first processed into sinter and pellets in order to ensure proper permeability of the charge in the blast furnace. The permeability is important for the reduction and combustion-related gases that are being formed, as well as for the hot metal to get at the bottom of the furnace. A portion of the

iron ore, together with aggregates, is first processed into 'pellets' (spheres) and 'sinter' (agglomerated chunks formed during smelting). These two forms of iron are then added to the blast furnace along with chunks of iron ore. Scrap iron is sometimes added as well. Auxiliaries such as sand and limestone are also added for the slag formation. The resulting slag is lighter than the hot metal. Slag formation is important because it removes undesired components from the hot metal. In addition to slag formed in the blast furnaces and BOF plants, slag is also formed in the process of hot metal desulphurisation. This slag is known in the Netherlands as 'ROZA' slag. Before the carbon content of the hot metal is reduced in an BOF plant, it is first processed to lower the concentration of primarily sulphur but also phosphorus in what is known as a desulphurisation ladle. This desulphurisation usually involves the addition of magnesium powder, calcium carbide, limestone or burnt lime [EIB, 2012, Corus, 2006 and Schrama et al., 2017] which results in the formation of (among other things) magnesium sulphide or calcium sulphide. In addition to the formation of slag, the various steps in the process also yield dust and sludge, which are channelled off through the flue gas cleaning system. A schematic representation of all raw material flows and the main by-products is shown in *Figure 3.2*.
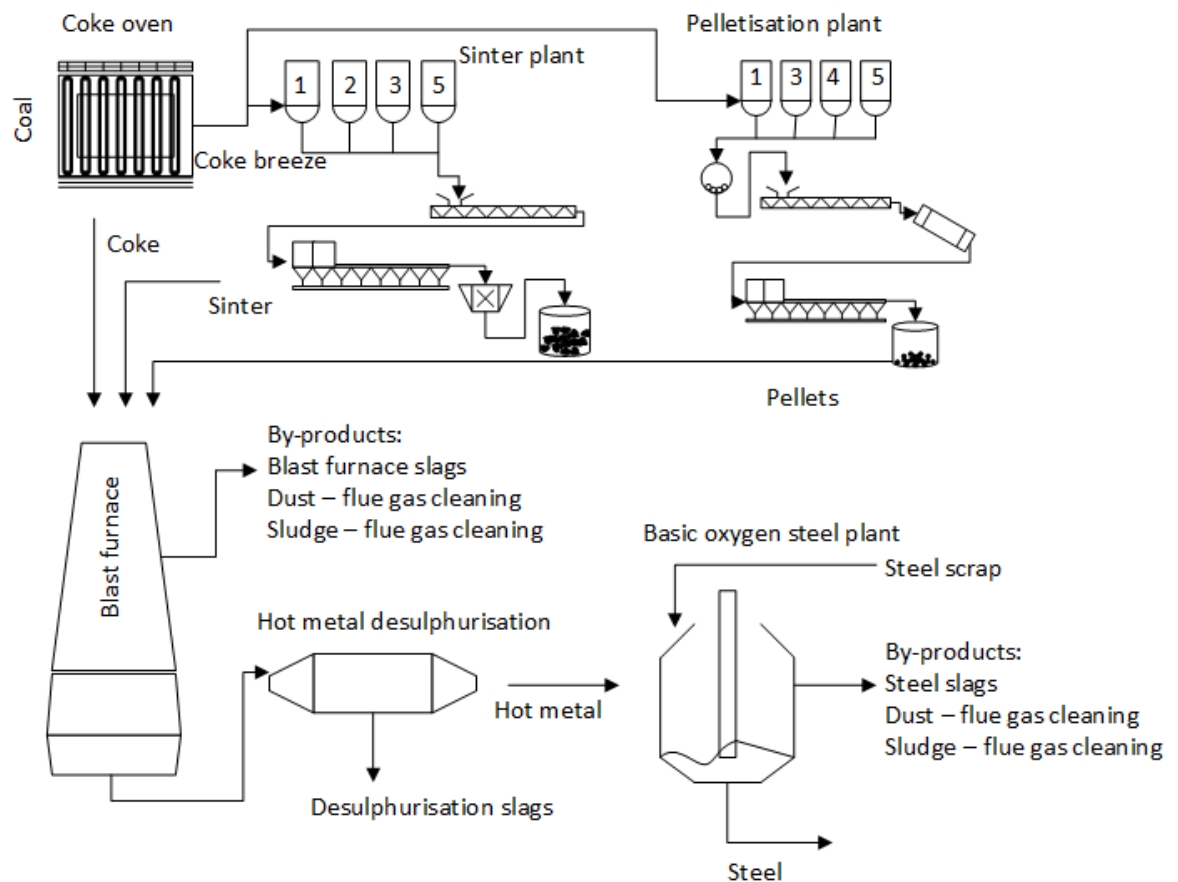
Figure 3.2 Raw materials used and by-products formed (steel slags, dust and sludge) at the production of in an integrated steel plant

In the BOF process, both crude iron (hot metal) that is produced in the blast furnaces and scrap are utilised as sources of iron. The scrap is added primarily to prevent the temperature of the hot metal in the converter from becoming too high. The reaction between pure oxygen and the carbon present in the hot metal can cause the temperature to exceed 1,700 °C.

The quantities of raw materials needed to produce one ton (1000 kg) of steel are shown in *Figure 3.3*. The data regarding the quantities of raw materials used are based on Harvey et al. [2020] and EIB [2012]. The data presented in both studies are quite similar. The data presented in Appendix B relate to the amount of 1000 kg for each (intermediate) product i.e. sinter, pellets and hot metal.

Coke oven	Sinter plant		Pellet plant	
	Iron ore	820	Iron ore	301
	Return sinter	253	Coke breeze	4
	Flux materials	169	Olivine	9
	Residues	160	Limestone	2
Coke breeze 49	Coke breeze	45	Bentonite	2
Coal 474			Quartzite	3
Coke 320				
Sinter 1009			Pellets 317	

Blast furnace		
Sinter	1009
Pellets	317
Cokes	320
Injection coal	137
Iron ores	113
Limestone	12
Quartzite	10

Quicklime 1

Hot metal desulphurisation   Hot metal 901

Basic oxygen steel plant	
Hot metal	901
Scrap	190
Limestone	65
Dolomite	11
Pellets	5

Steel 1000

Figure 3.3 Quantities of raw materials used (in kg) when producing 1,000 kg of steel in an integrated steel plant

Table 3.1 below sets out the amount of chromium per ton of steel introduced through the various raw materials used in the BOF process. Data on chromium concentrations in steel scrap are presented in section 2.4. Background information on the other raw materials is included in Appendix B. Appendix B also includes the mass balance for chromium in

all sub-processes, e.g. the production of coke, sinter, pellets, crude steel and steel.

Table 3.1 Quantity of raw materials used and chromium flows in connection with the production of 1,000 kg of steel in the BOF plant. Background information on selected chromium concentrations can be found in section 2.4 for steel scrap and for the other raw materials in Appendix B.

Raw material	Quantity (kg)	Cr concentration (ppm)	Mass of Cr (g)
Hot metal	901	69	61.9
Scrap	190	1,000	190
Pellets	5	56	0.28
Burnt lime	64.8	11	0.713
Sintered dolomite	10.9	21	0.229
Total	**1,172**		**253,1**

A complete overview of the flows of chromium through the raw materials used in an integrated steel plant is shown in Figure 3.4 (chromium in each material stream per 1000 kg of steel produced). In this scheme chromium losses via slag and emissions are not included as separate flows. As will be shown in section 3.2.5. when discussing the losses from the BOF process, losses via emission and dust collected from the off gases can be neglected compared to slag. The study by Persson [2019] also shows that losses via off gases can be neglected. Key in the assessment of the amount of chromium is the removal of chromium by slag. Figure 3.4 shows the range of chromium content in hot metal and the produced steel based on the available data found in literature.
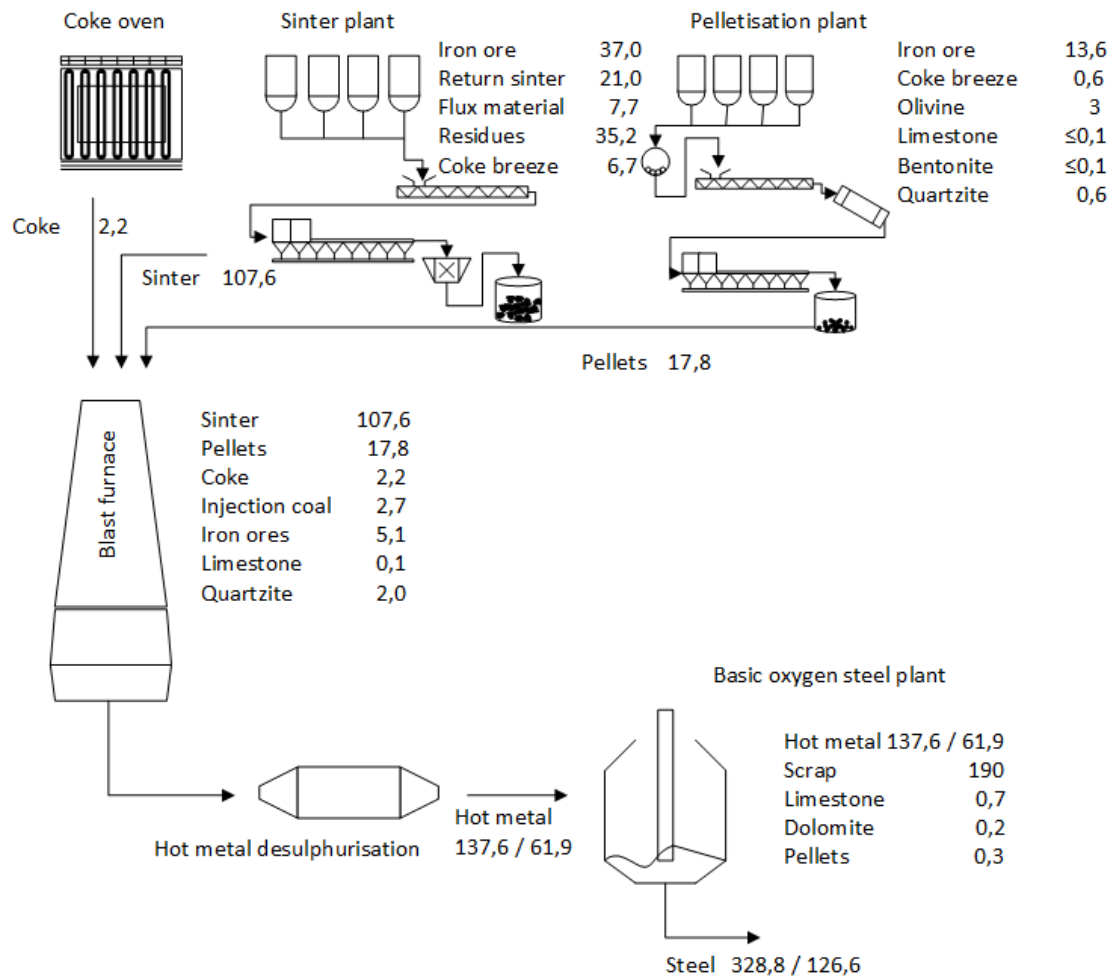
Figure 3.4 Chromium input through raw materials (g) when producing 1,000 kg of steel in an integrated steel plant. The concentrations to the left of the hyphen do not take removal through slag into account; the figures to the right of the hyphen are based on the assumption of 50% removal in the BOF and 55% removal in the blast furnace.

Part of the chromium that enters the blast furnace is removed by the slag. According to Corus [2006] about 50 -60% of the chromium that is present in the iron ore ends up in the slag. In a study on the chromium mass flow in the blast furnace [Trinkel et al., 2015] it was shown that between 84% and 95% of chromium is transferred to the hot metal and only 1.2 % to the waste gases. Assuming that 55% of the chromium is removed, the chromium content in the hot metal will be about 69 ppm. Trinkel et al. [2015] conclude that chromium is almost exclusively transferred to the hot metal. When assuming no removal in the blast furnace, the chromium content in the hot metal is 153 ppm. The average hot metal chromium content resulting from the data presented in Trinkel et al. [2015] of 245 ppm is nearly twice as high. Lower chromium contents of around 90 ppm are reported by Wang et al. [2022].

The degree to which the elements are removed in the BOF depends primarily on the extent to which they will be oxidised. This, in turn, will

depend on process conditions such as the temperature and the quantity of oxygen introduced (redox conditions) and how basic the slag is (its basicity). Although different definitions exist for the basicity of slag, it is typically expressed as the ratio of the sum of calcium and magnesium oxide on one hand and silicon oxide on the other: $(CaO+MgO)/SiO_2$. If the ratio is higher than one, the slag is basic; if the ratio is less than one, the slag is acidic. The degree to which alloying elements become oxidised and are removed also depends on the composition of the iron, which elements are present and in which proportions. This is because the least noble elements will be the first to react with oxygen. Chromium and manganese, for example, are less noble than iron. Particularly important is the extent to which an element reacts with oxygen compared to the extent to which iron does so. While a certain amount of iron loss due to oxidation is inevitable, the process is designed to minimise such loss. The oxidation of chromium and the degree to which it is absorbed by the slag is discussed in greater detail in section 4.

For the reasons explained above, the degree to which chromium is extracted from the molten steel through slag can vary quite strongly, from 5% to 70% for electric arc furnaces [Reijnders, 2016]. This means that between 95 and 30% of the chromium remains in the iron. Based on this range an average 50% removal can be assumed, which matches the split of about 50/50 for the chromium partitioning in the BOF between slag and hot metal obtained from the study by Persson [2019]. Furthermore, losses of chromium via off-gases are not included in the mass balance, because they can be neglected compared to amounts lost via slag. Based on these extraction percentages, the chromium content in the produced steel may vary from 127 ppm assuming 55% removal in the blast furnace and 50% in the BOF to 329 ppm if no chromium is assumed to have been extracted through slag formation neither in the BF nor in the BOF. The chromium contents for crude steel reported by Persson [2019], ranging from 207 ppm to 280 ppm, fall within our estimated range. It can be concluded that the most important factors that influence the final chromium content are the chromium content of the hot metal and scrap and the degree to which that chromium is extracted through slags.

Intermezzo:

According to an article on TotalMateria (2022), there is a linear relation between the ratio of the quantity of chromium in the slag relates to that in the liquid metal and the iron oxide content in slag in case of BOF and electric arc furnace heats. The proportionality constant ranges from 0.28 to 0.5.
$([Cr]\_slag/[Cr]\_metal = 0.3 \times \%FeO$
(See
https://www.totalmateria.com/page.aspx?ID=CheckArticle&site=kts&LN=NL&NM=220)
The advantage of this method is that the iron content is virtually always known in studies that examine the composition of steel slag. Because sufficient data was found on the chromium concentration in steel slag, this method has not been applied in this study.

The above chromium balance for the production of steel in an BOF plant shows that the scrap accounts for the majority of chromium input: 75%. The hot metal accounts for about 25%. The chromium contribution of the remaining raw materials and auxiliaries is negligible.

These results clearly show the relevance of the quality of the steel scrap. According to the specifications for steel scrap, the chromium content in practice is less than 0.25%. Well-sorted scrap contains approximately 0.05% chromium, see section 2.4.4. If these concentrations are taken, then the scrap accounts for 60% to 88% and the concentration in the steel will be between 538 and 158 ppm. It should be noted that this these numbers dos not yet take into account the extraction removal of chromium during the BOF process. The removal via slag however does not affect the relative contributions of the various sources.

3.4.2 *Resulting by-products and waste materials*
3.4.2.1 Quantity of by-products formed

The tables below provide an overview of the quantities of residues that are formed in the process of producing steel by means of an integrated production process. Dust is collected during the production of sinter and pellets. Sludge is formed in the course of wet-filtering dust from flue gases (possibly at sinter and pellet plants and BOF primary gas cleaning). A part of these residues are reused in the production of sinter. Dust is formed and partly extracted during the production of coke as well.

Table 3.2 provides an overview of the quantity of dust and sludge collected during the production of sinter [EIB, 2012]. Most sinter plants are operated with fully closed dust cycles. These means that the majority of the dust collected is returned back to the sinter production. Therefore dust collected from sinters plants should not be considered as losses from the integrated steel production process. Only releases of dust to air, which are in the range of 559 – 41 grams per ton of sinter should be regarded. However, the chromium emissions, which are in the range of 125 – 4 mg per ton of sinter are negligible compared to a chromium content of little more than 100 grams per ton of sinter. With regard to the production of pellets and coke, the BREF [EIB, 2012] provides no data on the quantities of dust collected. The captured dust from pellet production can be fed directly to the mixing stage as it has the same composition as the raw material [EIB, 2012]. So the same as for sinter plants, only releases of dust to air, which are in the range of 150 – 14 grams per ton of pellets should in principle be regarded as losses. The chromium (total) emissions to air are 5-22 mg per ton product, which is negligible compared to the total chromium content in pellets of somewhat less than 60 grams per ton of pellets. Therefore, the losses of chromium to air will be neglected in the chromium balance.

Table 3.2 Quantity of dust and sludge formed during the production of sinter (kg per ton sinter)

Process	Dust			Sludge[1]			Reference
	Min.	Max.	Typical	Min.	Max.	Typical	
Sinter	171	3,641	1,906	473	4,492	2,482	EIB (2012)
Blast furnace	4.0	23.1	13.5	2.0	22.3	12.2	EIB (2012)

[1] This concerns sludge from wet waste gas treatment systems. In 2012 there was only one plant in Europe operating such a system, which might be shut down in the medium term. Sludge from sinter plants is therefore considered to be not relevant.

With emissions of chromium to air in the range of tens of milligrams per ton of hot metal produced in the blast furnace (emissions from the cast house to air range from 10.4 to 2.8 mg per ton, [EIB, 2012]) and an amount of around 60 g per tonne of hot metal (see Table 3.1), the emissions to air also are negligible. The amounts of dust and sludge generated should be added because usually a tow stage (dry followed by wet) flue gas treatment is applied. Somewhat less than 2/3rd of the dust and sludge collected from the blast furnace gas treatment is recycled on-site. The remainder largely goes to landfills.

As previously discussed, in addition to the blast furnace slag, slag is also formed during further processing as part of BOF production. This results in so-called BOF or LD slag. Generally, 300 kg of slag is produced and 20 kg of dust and sludge is collected for every ton of hot metal (see Table 3.3). In steel production, 125 kg slag and 22 kg dust and sludge are created per ton of steel produced (see Table 3.4).

Table 3.3 Quantity of slag and dust formed and collected during the production of hot metal in the blast furnace (kg per ton hot metal)

Reference	Slag			Dust and sludge		
	Min.	Max.	Typical	Min.	Max.	Typical
EIB (2012)	150	346.6	248	6.0	45.4	26
Harvey (2020)	160	421	291			
Rentz et al. (1997)			308			19
Ene and Pantelica (2010)			420			7
Orowho (2014)			275			20.3
Chosen value			300			20

Table 3.4 Quantity of slag and dust formed during the production of steel (kg per ton steel)

Reference	Slag			Dust and sludge		
	Min.	Max.	Average	Min.	Max.	Average
EIB (2012)	85	165	125	0.75	24	12
Harvey (2020)	50	206	128			
Rentz et al. (1997)			111.3			30
Orowho (2014)			126			22.9
Chosen value			125			22

During the desulphurisation of the hot metal (and before the further processing commences in the BOF plant) a quantity of desulphurisation slag is produced in the range of 3 to 40 kg per ton of molten steel [EIB, 2012].

In the secondary metallurgical process, the final step in the production of steel, secondary slag (also known as ladle furnace slag or white slag) is formed. According to the BREF [EIB, 2012], the quantity of ladle furnace slag formed ranges from 9 to 15 kg per ton of steel. The total quantity of slag that will have been formed after the production of hot metal is set out in Table 3.5 below.

Table 3.5 Quantity of by-products created during the BOF process

By-products	Quantity (kg/ton)
BOF slag	125
BOF dust and sludge	22
ROZA slag	22
Ladle furnace slag	12
Total	181

3.4.2.2 Chromium content of slag, dust and sediment from flue gas treatment
This sub-section addresses the results of the literature review aimed at identifying the chromium content in the various by-products. The production process results not only in slag, but also in dust. A portion of this dust is collected through vent systems and can be extracted from the flue gases using different kinds of filters. In some installations, water is used to remove dust from the flue gases, resulting in the formation of sludge. In principle, the sludge formed in this manner will have the same composition as the dust. That said, a portion of the oxides and salts present in the dust may dissolve in water and be emitted by that route. This does not affect the chromium balance. For this reason, the concentrations in the collected dust will serve as the basis for drawing up the chromium balance. In the interest of completeness, measured concentrations in the sludge are included in the overview.

Appendix C contains the chromium concentrations in slag and in the dust and sludge resulting from blast furnace process, the desulphurisation of hot metal and the BOF process, as found in the literature.

Based on the data set out in Appendix C, the typical *chromium concentrations for the dust and slag* produced in the course of the different production processes are as follows. For the purpose of calculating the concentrations one could typically expect to find, extremes (factor 10 higher or lower than the median) and values displayed as 'less than' (<) have been excluded from consideration, assuming that the figures are not representative of the standard process:
- Blast furnace
  - Slag: 60 ppm

- o Dust: 740 ppm
- Desulphurisation
  - o Slag: 340 ppm
- BOF
  - o Slag: 3,110 ppm
  - o Dust: 260 ppm
  - o Sludge: 220 ppm
- Ladle furnace
  - o Slag: 80 ppm

As expected, the concentrations in the sludge and the captured dust were similar (BOF process). It is also notable that the chromium content in the dust from the blast furnaces is higher than in the dust from the BOF process. The chromium content in the slag formed by the BOF process, on the other hand, is much higher than that of the slag from the blast furnace process. This could be explained by the conditions under which the BOF process takes place. These are designed to remove chromium and other undesirable elements from the steel via slag. It could also have to do with the higher input of chromium through the added steel scrap. The blast furnace process also results in a larger quantity of slag because it involves a larger quantity of slag forming agents, resulting in dilution.

In terms of total chromium concentration, the ladle furnace slag appears to fall into two groups; see Appendix C. In one group, values found were larger than 1,000 ppm with an average value of 8,300 ppm. The other group had an average value of 180 ppm. This may have to do with the type of steel being produced. Higher values are to be expected in connection with the production of steel alloys such as stainless steel, which involves the use of scrap with a higher chromium content and (potentially) the addition of other alloying elements. The average of all reported values is 4,700 ppm. Because the majority of steel produced by primary steel production is either unalloyed or low-alloy steel, in making the mass balance a relatively low concentration of 80 ppm (taken from Kolszár et al. [2016]) based on unalloyed steel is assumed.
Five samples of hot metal desulphurisation slag (ROZA slag) were found to have an average chromium concentration of 0.05% Cr_2O_3, or in other words 340 ppm chromium [Schophuizen, 2018].

3.4.3 Chromium balance of BOF steel production
In this section, we use the data on the quantities of raw materials used, the amounts of by-products produced and the chromium concentrations of the various material flows to draw up a chromium balance. This has allowed us to arrive at an estimate of the chromium content of the steel produced, as well as the respective contributions of the various raw materials.

The quantities of by-products produced and the average chromium content present in those by-products provide a picture of the total amount of chromium present in these materials. The calculated quantities are listed in Table 3.6. These quantities provide only a general idea of the relative proportions. It appears that the total calculated quantity in the by-products is higher than the quantity that entered the process through the raw materials. One explanation for this is that the

calculations are based on average quantities and concentrations. Another reason is the uncertainty in the amount of chromium in the hot metal that is produced in the blast furnace. Assuming no removal, the chromium content in the hot metal is about 153 ppm. Chromium contents found in literature range from around 90 ppm [Wang et al., 2022] to 361 ppm [Trinkel et al. 2015]. The discrepancies can partly be related back to the degree of removal by the blast furnace slags. Based on Trinkel et al. [2015] only 4 to 15% of the chromium is removed by the slags. While according to Corus [2006] about 50 - 60% of the chromium that is present in the iron ore ends up in the slag. In the latter case the chromium content in the hot metal would be around 69 ppm. The mass balance around the BOF is nearly closed when using the average of the hot metal chromium contents presented in Trinkel et al. [2015] of 245 ppm, excluding the amount in the left in the crude steel leaving the BOF. For comparison the total chromium input derived in the current study (section 3.4.1) are provided as well. The good match should in this case be considered as more or less a coincidence, considering the large uncertainties. The data show the uncertainty in and importance of the chromium content in the hot metal. In order to able to balance the inflow and outflow, the quantities and concentrations of the various streams need to be determined carefully for a specific production location and should not be based on average figures for various production facilities. Even then, it will be difficult to close the balance and detailed information will be required.

Table 3.6 Quantity of chromium in by-products of the BOF process, per ton of steel compared to the chromium input.

Flows	Quantity (kg/ton)	Cr content (ppm)	Quantity of chromium (g)
Output			
BOF slag	125	3,110	388.8
BOF dust and sludge	22	260	5.7
ROZA slag	22	340	7.3
Ladle furnace slag	12	80	1.1
Emissions into the air			Negligible[6]
Total output			**402.7**
Input through raw materials			
Applying the average concentration in hot metal (Trinkel et al. [2015])			420.0
No removal via BF-slag, see section 3.4.1			328.8
55% removal via BF-slag, see section 3.4.1			253.1

Of the by-products, slag is produced in the greatest quantities and makes up around 70% of the total. Slag also accounts for the majority of the chromium present, with about 96% of the total amount. As indicated in section 3.2.4 emission to air can neglected in the chromium

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[6] Total emissions from integrated steel production is approximately 40 mg per ton of steel. This is negligible in comparison to the other outgoing flows, of which ladle furnace slag accounts for the smallest portion: 1,100 mg per ton of steel. Emissions into the air are described in Table 3.7

balance. Dusts and sludges are generally re-used in the integrated steel process (especially sinter and pellet dust).

The quantity of chromium in slag can also be calculated in a different way, by assuming a specific removal efficiency in the converter of the BOF plant. After all, one of the primary functions of slag is to remove impurities such as certain metallic elements from the molten steel. The values for removal through slag mentioned in the literature range from 70 to 5% [Reinders, 2016]. If it assumed that 50% of the chromium present is removed through slag formation, the chromium content in the slag (after subtracting the quantity in the remaining by-products) will be approximately 100 ppm (0.01%). This is roughly equal to the 15th percentile of values found in the literature. The lower and upper limits, if we assume extraction percentages of 5% and 70%, are 96 ppm and 1,340 ppm respectively. Values found in the literature are between 90 ppm [Ene and Pantelica, 2011] and 8,550 ppm [Saqlain et al., 2018]. Persson [2019] reports chromium contents for BOF-slag ranging from 1605 – 2135 ppm, which closely match the measured content of 2000 ppm reported by [SWECO, 2020].

3.4.4 *Emissions and emission factors*
This section addresses the emissions of chromium into the environment (to air and water) during the production of primary steel using the integrated production process. First some general data on emissions and emission factors for the whole production process and the separate process units will be presented. Also specifically addressed in this section are the emissions resulting from the BOF process with the focus on the emissions related to the use of steel scrap.

3.4.4.1 General emissions
There are a total of 27 integrated steel plants in the EU and the United Kingdom. There is only one such plant located in the Netherlands, Tata Steel in Velsen-Noord. The historical emission data on chromium for this site (supplied by the company) are included in the Dutch emissions register (ER, 2022). More detailed data on the chromium emissions can be found in the digital annual environmental report (e-MJV, 2020). This report contains the emissions to air (and water) generated by the various plants at the production location in Velzen-Noord. With regard to the emissions to water, there is no break-down to the various installations. Instead, only the total emissions for the whole site are given. The total emissions to air and water over the years are displayed in Table 3.7. Figure 3.5 shows the share of the total chromium emissions to air caused by each factory.

Since the 1990s, chromium emissions to both air and water have decreased strongly: from over 1,400 kg and 1,300 kg per year, respectively, to around 186 kg and 187 kg in 2019. The sintering plant is currently the largest source of emissions, with emissions to air of 100.3 kg in 2019 (54%). The contribution from the BOF plant is similar to that of the blast furnaces at around 10%, while the pellet plant accounts for a slightly larger portion (15%). The coking plant contributed another 3% to chromium emissions [e-MJV, 2020].
At the Tata Steel site in Velsen-Noord, there is also a Tata Steel Packaging (TSP) plant, where rolls of sheet steel are processed for the

packaging industry. This plant includes tinning and chrome-plating facilities, where a layer of tin or chromium is deposited onto the sheet steel using an electrical current (electroplating). The chrome plating installation emits chromium(VI) into the environment.

In 2019, the TSP plant was still using chromium(VI) for chrome electroplating. Today, the plant is transitioning to a different process for chrome plating that utilises trivalent chromium instead. Thanks to the new chrome-plating process, the use of electrolytic solution containing chromium(VI) will eventually cease [ODNZKG, 2015 and ODNZKG, 2017]. In 2019, 7.8 kg of chromium(VI) was emitted into the air [e-MJV, 2020].

Table 3.7 Emissions of chromium into air and water (kg/year) by Tata Steel in the period 1990–2019 [ER, 2022]

Year	Air	Load in water
1990	1,432	1,300
1995	1,629	362
2000	448	671
2005	642.4	109.7
2010	629.1	82.2
2015	295.3	107.5
2018	187.2	-
2019	186.3	187.4
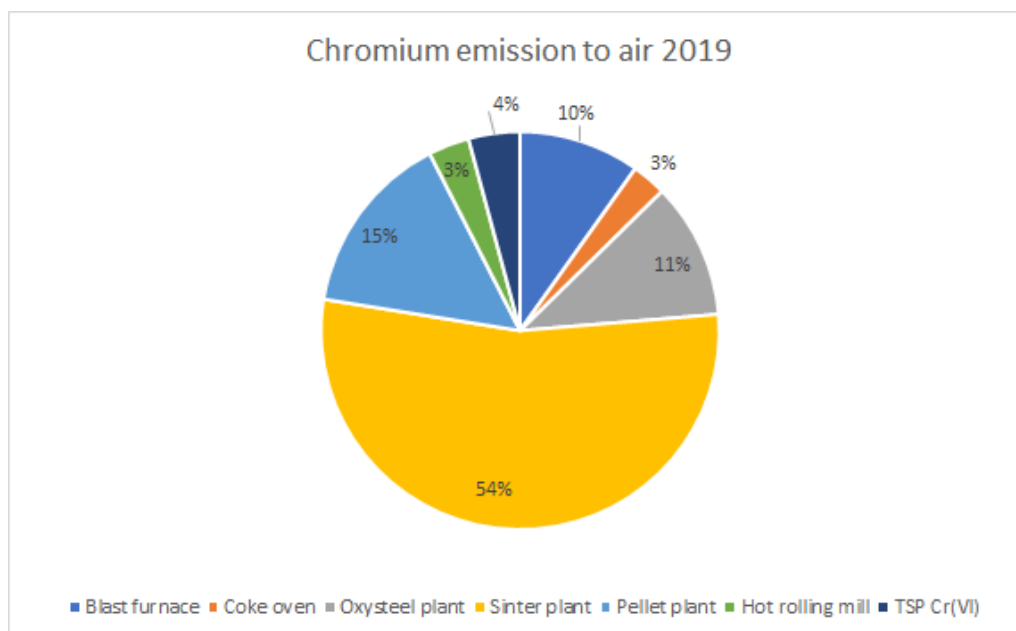
Figure 3.5 Share of the total chromium emissions to air caused by each of the various production processes at Tata Steel in Velsen-Noord in 2019. Emission figures according to e-MJV [2020].

The emissions and the quantities of product produced by each plant in 2019 are shown in Table 3.8. From this information, specific emission factors can be calculated. Emission factors are expressed based on the quantity of product produced by each sub-process, rather than based on

the quantity of final product (steel) produced by the entire process. For comparison, the range of emissions factors for air as reported in EIB (2012) are provided.

According to the e-MJV, 5.98 Mton of blast furnace hot metal and 6.86 Mton of steel were produced in 2019. The quantities of coke, sinter and pellets produced are given as well.

The quantities of sinter and pellets are not listed separately in the e-MJV; instead, only the total quantity is given. In order to make a distinction, 75% of the total amount is assumed to be sinter and 25% pellets (EIB, 2012). It is also assumed that all steel produced is processed by the hot-rolling mill.

Table 3.8 Emissions and calculated emission factors for total chromium to air from the various production processes at Tata Steel in Velsen-Noord

Source	Emission of chromium to air (kg)	Production (ton)	Emission factor of Tata (mg/ton)	Emission factor from EIB [2012] (mg/ton)
Sintering plants	100.3	6,139,821	16.3	3.6–125.1
Pellet plant	27.9	2,046,607	13.6	5.1–22.4
Coking plants	5.2	1,987,828	2.6	-
Blast furnaces	18.3	5,984,226	3.1	2.8–10.4
BOF plant	20.6	6,857,395	3.0	10–75
Hot-rolling mill	6.2	6,857,395	0.9	

The emissions from the chrome-plating plant are excluded from consideration because they are not part of the steel production process. EIB [2012] does not include emissions factors for chromium in for the production of coke. It is also unclear whether the emissions factors given in the BREF [EIB, 2012] for the steel plant also include the emissions from the hot-rolling mill. Assuming those emissions have been included in the emissions factors that are reported in the BREF, the total chromium emissions of the steel plant reported in the e-MJV still seem to be low: 2.5 times lower, than the lowest emissions factor reported in the BREF. The reasons for this low figure are unclear, there might be several reasons, such as the quality of the scrap that is used, the way the flue gas is cleaned or the representativeness of the measurement samples. Except for the pellet plant (whose emissions factor is average), the emissions factors for the different production processes of Tata Steel in Velsen-Noord are lower than the European average.

3.4.4.2   Emission from BOF operations
The operation of a BOF is semi-continuous. A complete cycle consists of the following phases: charging scrap and molten hot metal, oxygen blowing, sampling and temperature recording, and tapping [EIB, 2012]. During the process, a number of auxiliary materials and alloying metals are added to adapt the steel quality and to form slag. During charging and tapping, the converter is tilted. During oxygen blowing, the converter is placed in an upright position.

The oxygen steelmaking process generates considerable quantities of dust during the charging of scrap and hot metal, oxygen blowing, and during the tapping of slag and liquid steel. The process of loading hot metal in the BOF is a critical step with regard to air emissions and occupational exposure. All steelmaking plants in the EU have taken measures to reduce dust emissions.

Secondary emissions composition
Charging: Depending on the quality of the scrap used various organic pollutants such as PCB and chlorobenzenes resulting from the thermal degradation of organic materials (oils, paints, lubricants or plastics) may be present in the emissions from the charging of scrap and when the hot metal is poured on top of the charged scrap [EIB, 2012]. Considering the temperature of the hot metal of about 1200 °C [Diaz et al., 2019] it is likely that all of the organic material is burned (off) during the hot metal charging.

Primary emissions composition
Oxygen blowing: The gases produced during oxygen blowing (converter gas) contain large amounts of carbon monoxide. In most steelmaking plants, measures have been taken to recover the converter gas and use it as an energy source.

Metal oxides are released mainly when the load has been melted and when the temperature further increases as oxygen is introduced. The addition of oxygen also results in agitation of the molten metal bath. Elements and oxides present in the smelt can evaporate during the smelting process. The degree of vapourisation determines how an element will be distributed across the flue gas, solid residue (such as slag and dust particles) and the molten metal. Elements can be classified according to the degree to which they vaporise and are distributed across the gas phase, finer particulates such as fly ash and coarser particles. The melting point of a given element provides an indication of its classification. The melting point of chromium is 2,671 °C, which is considerably higher than the standard processing temperature in an electric arc furnace (1,600 °C). Compared to lead and zinc, which are known to produce dust containing condensed metal vapours, the melting point of chromium is high. In terms of volatility, the element chromium belongs to a category between the group of elements (iron, manganese and magnesium) that do not vaporise and for the most part remain bonded to coarser, solid particles, and the group of elements such as cadmium, zinc and lead that become partially vaporised (semi-volatile) and tend to attach themselves to the finer particulates in dust [Clarke and Sloss, 1992 and Lau et al., 2022]. However, a certain degree of vaporisation may occur, particularly in high-temperature zones such as the electric arc zone, the oxygen blowing zone and the zone where reduction using carbon takes place. For these reasons, the dust is expected to contain very little or no condensed metallic chromium. The chromium present will primarily be found in metal droplets of the molten scrap and dust created by the formation of slag. According to Albertson [2013] and Rentz et al. [1997], gaseous chromium oxides may be formed under the process temperatures and oxidative atmosphere typically present during steel production.

Types of secondary and primary dedusting operations
Dust that is emitted during all of the above-mentioned processes needs to be captured and filtered to meet environmental quality standards. During charging or tapping operations, the converter is tilted. A 'secondary ventilation' and dedusting system, is often installed to abate the dust emissions that occur at this stage. The secondary ventilation system usually consists of a canopy hood just above the converter in the tilted position and a doghouse (furnace enclosure) around the remaining 3/4 of the converter. For these secondary emissions, generally dry techniques such as bag filters and dry ESP are used.

During oxygen blowing, the converter is in the upright position with the hood of the primary capture system close to the converter mouth. The primary system captures and treats the converter gas that is released during oxygen blowing. The secondary system extracts part of the primary emissions that are not captured by the primary ventilation system. Usually, dust is removed from the primary BOF gas using venturi scrubber.

Diffuse emissions occur from all of the above-mentioned processes whenever the emissions are not fully captured. Diffusely emitted dusts end-up in the converter hall where they are partially deposited or they escape via roof openings, windows and doors. Diffuse emissions are furthermore very relevant with regard to occupational exposure. In order to avoid diffuse emissions as much as possible, the primary and, in particular, the secondary extraction system should be optimised. Optionally, a roof extraction system (tertiary system) can be installed to capture the emissions that are not capture by the primary and secondary systems.. Tata Steel in Velzen-Noord is currently building a third system or so-called tertiary system in order to minimise the emissions to the environment. This tertiary system is a combination an extraction unit combined with a fabric filter installation.

Capture and filter efficiencies of dedusting operations
Capture efficiencies of the primary system can be calculated from the data presented in table 7.6 on page 374 of the BREF [EIB, 2012]. The primary system captures 12 – 23 kg dust per ton liquid steel. The remaining amount of dust emitted is 0.3 to 55 gram per ton of steel produced. This would mean that more than 99% of the dust going through the primary extraction system during oxygen blowing is filtered. As stated in the BREF, primary emissions such as the emissions formed during oxygen blowing are much easier to capture and have an (capture) efficiency of around 90% or higher (up to 99%) [EIB, 2012]. Data provided in section 7.2.2.1.2 of EIB [2012] suggest that the capture efficiency of the primary dedusting system is in the range of 96 to 98%.

Also relevant are the secondary emissions resulting from scrap charging, hot metal charging and the emissions during tapping. The unabated emissions at this stage are in the range of 200 to 1000 gram per ton of liquid steel produced as presented in table 7.6 of the BREF [EIB, 2012]. The total amount that is not caught by the enclosure and the amount that passes the filters totals up to 10 – 180 gram per ton of steel. Based on this the efficiency for capturing the emission from charging and

tapping is in the range of 95 to 85%. The numbers also show that secondary emissions are probably more critical with regard to air emissions than the primary emissions. More detail information on capture efficiencies is found in Table 7.20 of the BREF [EIB, 2012]. The degree to which it is possible to capture dust depends strongly on the phase of the process in which the dust is formed. The capture efficiency of secondary emissions that are formed during the loading of the scrap (24–64%) and the tapping of the molten steel and the slag (49–55%) is the lowest. For dust generated during charging of the hot metal on top of the scrap, capture efficiencies of between 89-94% can be achieved. These data do not seem to be fully in line with other information presented in the BREF stating that the capture rate of the secondary dedusting system is significantly higher, between 93 and 99.6%. An explanation might be that the bulk of the dust is generated during charging of the hot metal on top of the scrap. Even then, capture rates of between 93 to 99.6% seem to be rather high. We didn't find any literature data, regarding the contribution of each process step to the total dust emissions, or rather the unabated dust emissions resulting from each step, that would allows us to calculate the overall emission capture efficiency for the BOF process from the individual steps.

Emissions that escape the primary and secondary capture systems and are released into the production hall – the tertiary emissions – can be collected by an additional capture system in order to prevent them from being released to outside air. The capture efficiency of the tertiary system is approximately 50%, as reported by ODNZKG [2022] and Tata Steel [2022].

3.5 Electric arc furnace (EAF) and the induction furnace

3.5.1 Introduction
This section deals with two other type furnaces used in the production of steel and steel products, the electric arc furnace (EAF) and the induction furnace. These production processes fully or partly use steel scrap as a raw material. The direct smelting of (secondary) materials which contain iron, such as scrap in steelmaking is usually performed in electric arc furnaces. Ferrous foundries also use selected iron and steel scrap and pig iron as starting materials, besides internal return material [EIB, 2022]. Foundries use different types of furnaces such as induction furnaces and including EAFs. EAFs are thus both used in secondary steelmaking and by foundries which also to a certain extent use steel scrap as a raw material. In this section, we focus on electric arc and induction furnaces because EAFs play an important role in (secondary) steelmaking using scrap that to some extent may possibly be contaminated with chromium(VI), and because the induction furnace is applied in a Dutch plant dedicated to processing contaminated scrap. This section specifically addresses the use of raw materials, the formation of by-products and the emission(s) of chromium of EAFs and induction furnaces.

The term 'secondary steel industry' refers to the branch of industry in which steel is produced primarily from ferrous (iron and steel) scrap. The production of secondary steel usually involves the use of electric arc furnaces (EAFs). As previously stated, electric arc furnaces are also used

in primary steel production to a limited extent using hot metal and DRI by a rather small number of operators EIB [2012]. Besides scrap, that process relies mainly on direct reduced iron (DRI or sponge iron) for the production of steel.

With respect to the end-products, a distinction should be made between the production of ordinary carbon steel as well as low alloyed steel and high alloyed steels/stainless steels. The main reason is that high alloy steel is usually not coated with rust preventing primers and thus outside the scope of this report. Furthermore, for high alloyed and special steels, the operation sequence is more complex and tailor made for the end-products and higher amounts of alloying elements are used, which influences the composition of dusts and slags formed during the production process. In the EU, about 88 % of the steel production is carbon or low alloyed steel [EIB, 2012].

In addition to electric arc furnaces, other types of furnaces can also be used for melting down scrap during the production of new steel and their alloys. A portion of these activities take place at foundries where the molten iron is poured – i.e. cast – into a specific shape. This process is more of a batch operation, as compared to the continuous production that is used (in combination with rolling mills) to make steel sheets, rods and beams.

According to EIB [2012], the continuous production and processing of steel in the EU is conducted almost exclusively by means of the BOF (oxygen steel) process and the EAF process. Two-thirds of European steel is produced by means of the BOF process and the remaining one-third by means of the EAF process. In foundries steel is melted in electric arc, cupola furnaces and induction furnaces. Large steel foundries may use electric arc furnaces, but induction furnaces are more commonly used [EIB, 2022].

3.5.2 *Furnace process description and technique*
3.5.2.1 Electric arc furnaces (EAF)
The EAF is a batch-melting furnace consisting of a large bowl shaped refractory lined body with a dish shaped hearth. The furnace is covered by a refractory roof, which has ports for three graphite electrodes. The electrodes are supported by arms, which allow movement up and down. Most furnaces use roof charging: by moving the roof and electrodes aside, the furnace can be charged using a drop bottom charging bucket or a magnet. The metal charge is heated by an electric arc. The furnace is tapped by tilting it, forcing the metal to flow out through the spout [EIB, 2022].

Besides the use of scrap and sometimes pig iron or DRI as primary raw materials, alloying elements and slag forming agents (such as slaked lime and dolomite) are added. To remove oxygen, such as in the form of oxidised scrap (rust), and to prevent excessive oxidation, materials containing carbon are also added: coal or coke, for example. A portion of the carbon is supplied by the oxidation of the carbon electrodes. In order to bring the carbon concentration in the molten iron to the desired level, oxygen is added to the molten load (decarbonisation). The smelting in arc furnaces is followed by secondary metallurgical processes. These are usually carried out in a ladle furnace. In this stage,

subtle changes are made to the composition of the molten metal in order to arrive at the desired composition [Rentz et al., 1997].

3.5.2.2 Induction furnaces

The BREF document for smitheries and foundries provides a description of their operation and their applications [EIB, 2022]. An electrical induction furnace consists of a crucible – either cylindrical or bowl-shaped – lined with heatproof material and surrounded by electric coils. These coils produce a fluctuating electromagnetic field that heats the contents of the crucible. For safety reasons, the scrap must be cleaned and pre-heated before it is added to the furnace. This is necessary because any oil or moisture present on the scrap could cause an explosion in the furnace.

Besides smelting iron and steel, induction furnaces are also suitable for smelting aluminium, copper, lead and zinc. Iron foundries use pig iron, internally produced waste material and selected iron and steel scrap as raw materials. The composition of the selected external scrap depends on the desired final product. Alloying elements can also be added, potentially along with coke or graphite, to achieve the desired carbon content in the final product. During smelting, oxidation takes place where there is contact with air. The added carbon also serves to reduce the oxygen content by forming metal (iron) oxides and to prevent excessive oxidation of the iron (carbonisation). Unlike electric arc furnaces, the extraction of undesirable elements is not possible, or possible only to a limited degree, when using induction furnaces. As a result, the composition of the feed stock must be chosen with care when using an induction furnace. The purifying effect of induction furnaces on the smelt is limited by the small quantity of slag on the one hand, and on the other by the relatively small contact area between slag and molten metal [Goovaerts et al., 2001]. According to Gschwandtner and Fairchild [1990], it is possible to extract impurities from the load of molten metal (to a limited extent) by adding slag forming agents. If necessary, undesirable elements can be removed from the metal after smelting in an AOD furnace [EIB, 2022].

One advantage of induction furnaces (over EAFs) is that the emissions to air are lower [EIB, 2022]. This is primarily due to the more closed design of the furnace and the more closed nature of the process, which results in mainly primary emissions (emissions during smelting) that can be efficiently captured. The primary and other emissions are also lower because the use of induction furnaces does not involve refining the metal through the introduction of oxygen. The emissions are described in greater detail in sub-section 3.3.3.

When using induction furnaces (as previously stated), the extraction of undesirable elements is not possible, or possible only to a limited degree. For this reason, other raw materials such as limestone or dolomite are generally not added for slag formation. Other impurities – for instance organic material such as oil and paint residues – will burn in an induction furnace and be emitted as dust. The inorganic contaminants such asbestos will break down due to the high temperature, separate from the molten steel and then form slag together with other inorganic material such as sand and rust.

3.5.3 Chromium in raw materials and waste materials for EAFs

3.5.3.1 Electric arc furnaces

As indicated in the previous section, the raw materials and additives employed may vary based on the process used, the quality of the scrap and the desired final product.

The quantity of raw materials used in the production by means of electric arc furnaces is shown in Table 3.9 Quantity of raw materials used in electric arc furnaces for the production of 1,000 kg of steel. This data comes from the EIB [2012] and Rentz et al. [1997].

Table 3.9 Quantity of raw materials used in electric arc furnaces for the production of 1,000 kg of steel

Raw material	Quantity of raw material (kg)	
	Rentz (1997)	**BREF (2012)**
Scrap	1,105	1,136
Coal	14	16
Electrodes	3	4
Limestone[a]	55	83
Heatproof lining	8	32
Total	1,168	1,250

[a] Typically lime is used but in a few cases dolomite alone is used or combinations of dolomite and lime (e.g. weight proportion 63/37) [EIB, 2022]. For the calculations 100% limestone is assumed.

The quantities of chromium that enter the process through the raw materials have been calculated based on the chromium concentrations given earlier in this section and the quantities of raw materials as listed in EIB [2012]. With respect to scrap quality and consequently the chromium content it is important to note that different types of scrap are used. Generally, obsolete scrap which has a quite variable composition and may contain higher amounts of contaminants (e.g. Cr, Cu, Ni) are diluted with other clean íron units such as DRI or HBI or pig iron, or with scrap of much higher quality (i.e. prompt scrap). Some plants may actually decide to use mostly prompt scrap but that will cost much more. In most cases, obsolete scrap is diluted with clean iron units, which would lead to a lower chromium concentration in scrap. Considering this, the scrap quality will be important in chromium mass balance, which will be discussed at the end of this section. The calculations, the results of which are shown in Table 3.10, reveal that the chromium concentration in the final product is determined almost entirely (for >99%) by the chromium content in the scrap.

Table 3.10 Quantity of chromium in raw materials used to produce1,000 kg of steel in EAFs

Raw material	Quantity of raw material (kg)	Cr content (ppm)	Mass of Cr, based on BREF data (g)
Scrap	1,136	1,000	1,135.5
Coal	16	20	0.3
Electrodes	4	7[a]	0.03
Limestone[b]	83	11	0.9
Heatproof lining	32	-	
Total	1,250		1,136.4

[a] same chromium content as in cokes is assumed; [b] 100 percent limestone is assumed

As with the previously addressed blast furnace, steel and ladle furnace slag from primary steel production, slag is also formed by the use of electric arc furnaces and induction furnaces.

Table 3.11 sets out the chromium contents found in the literature for the slag and dust formed in electric arc furnaces when making steel with low (LAS/CS) and high (HAS/SS) concentrations of alloying elements. As previously stated, nickel and chromium are the most common choices for producing high-alloy steel such as stainless steel. Due to the higher chromium content in the scrap used (and potentially due to extra alloying elements being added to the molten material), the concentrations in the slag and dust are correspondingly higher. In connection with the production of high-alloy steel, the chromium content of the resulting slag is one-and-a-half to two times higher. With regard to the dust that is formed, the difference is even larger: around a factor of 10. It is also notable that with regard to unalloyed steel, the chromium concentrations in the dust are lower than the concentrations in the slag. At the production of alloyed steel, by contrast, the concentrations in the resulting dust are up to three times higher than that of the slag.

Table 3.11 Chromium content in EAF slag and EAF dust for low and high-alloy steel

EAF slag

Product	Cr content (%)	Reference
LAS/CS	1.0–2.1 (1.2)	Rentz et al. (1997)
	1.2	EIB (2012)
	1.8	Tossavainen et al. (2007)
	2.5	Horckmans et al. (2019)
	2.5	Bru et al. (2022)
Average	2.0	
HAS/SS	2.1	Rentz et al. (1997)
	1.4	EIB (2012), Table 8.7
	2.2	Tossavainen et al. (2007)
	2.3	Horckmans et al. (2019)
	2.0–4.8 (3.1)	Albertson (2013)
	5.5	Echterhof et al. (2011)
	4.4	Li and Xue (2019)
Average	3.0	

EAF dust

Product	Cr content (%)	Reference
LAS/CS	0.47	Omran and Fabritius (2017)
	0.20	Havlik et al. (2006)
	<0.1–0.26	Rizescu et al. (2010)
	0.30	Malecki et al. (2021)
	0.73	EIB (2012), Table 8.10
	0.21; 0.23	Simonyan et al. (2019)
Average	0.35	
HAS/SS	0.28–16.5	Ma and Garbers-Craig (2006)
	9.99	Ma and Garbers-Craig (2009)
	3.19	Omran and Fabritius (2017)
	2.09	EIB (2012), Table 8.11
	9.92	EIB (2012), Table 8.12
Average	6.7	

LAS/CS: low-alloy steel/carbon steel. HAS/SS: high-alloy steel/stainless steel. Each figure in parentheses is the average of four or more values.

The average chromium content in slag formed during the production of steel is 2% for high-alloy steel and 3% for low-alloy steel. With regard to dust, the concentrations are 0.35% for low-alloy steel and 6.7% for high-alloy steel. The concentrations in slag formed during the production of the two different types of steel are comparable, while the values for dust are obviously quite different.

For the chromium mass balance, the losses of chromium in the EAF-process via slag and dust emissions, which will be presented in the next sections, need to be taken into account. Losses are calculated taking the

average amount of slag, 165 kg/t (average of 60 -270 kg/t) and dust, 20 kg/t (average of 10-30 kg/t) produced by EAFs and the above mentioned chromium contents in slag and dust, results in 3.3 kg of chromium in slag and a maximum of 0.1 kg of chromium in dusts. The total amount of losses calculated in this ways appears to be higher than the total input. There is not much variation in the chromium content in the slags produced (minimum 1% and maximum 2.5%) so the imbalance rather seems to be caused by the amount of slag produced. To balance the amount of chromium input and output the amount of slag produced needs to be 53 kg/t. Most, likely the chromium content and the amount of slag are about 1.5% and 70 kg/t. On the other hand the chromium content in the steel scrap is highly variable and in general likely to be higher than the assumed 0.1%. Low steel scrap qualities may be more common in secondary steel making using electric arc furnaces.

3.5.3.2 Induction furnaces
In induction furnaces, virtually no fluxes are used; the slag is formed primarily by the oxides present in the scrap and the weathering of the heatproof lining of the furnace. The amount of chromium in steel produced in an induction furnace will therefore depend almost entirely on the chromium content of the scrap and on the share of scrap versus pig iron used.

The amount of slag produced by induction furnaces is between 10- 20 kg per ton metal charge. The amount of slag produced depends on the quality of the charge material [EIB, 2005].

3.5.4 Emissions and emission factors
3.5.4.1 Electric arc furnaces (EAFs)
Dust is formed during the various steps of the process, i.e. loading the furnace, smelting the scrap, extracting impurities by blowing in oxygen and tapping the molten metal.

Dust is formed primarily at the start of the production process, when the scrap is loaded into the furnace, and at the start of the smelting process, when the electrodes are lowered into the furnace and the scrap is heated and continues to melt. The scrap is generally added to the furnace in batches (2 or 3 portions). While scrap is being added, the lid of the furnace is removed entirely. At this point, a hot furnace already contains molten steel from the earlier loads (molten heel). For this reason, the scrap is pre-heated before being brought into contact with the molten steel. The combustion of any flammable materials present in the scrap (such as oil or lubricant) results in plumes of smoke consisting of burnt and partially burnt organic material and dust particles. The lid with the electrodes is then placed back on the furnace. In the next step, when the electrodes are lowered into the furnace, dust is still being formed by partially combusted material because the added scrap must be further heated in order to melt. At this point, the lid of the furnace is usually still ajar, which makes it more difficult to efficiently capture vapours and dust. Dust formation also occurs when the lid is closed and the scrap has been fully melted and is then further heated while oxygen is added to lower the carbon content (decarbonisation). Smoke is also formed during this phase, especially due to the metal oxides being

released. Smoke development strongly increases during the addition of oxygen. The addition of the aggregates causes a slight temporary increase in dust formation. Relatively minor quantities of dust are emitted when the furnace is emptied.

The emissions released during the smelting process – specifically when the lid is placed back on the furnace lid – are known as primary emissions. Secondary emissions are the emissions that are released when loading and emptying the furnace. With regard to the air treatment systems, they are referred to as the secondary air treatment system and the primary capture system. Primary emissions generated during the melting can be collected by direct extraction from the furnace. Secondary emission can be captured by hoods or placing the furnace in a dog-house. Emissions that escape from the secondary system are released into the production hall. It is possible to install a tertiary air cleaning system in order to reduce emissions from the hall into the outside environment Alternatively in combination with furnace extraction, the entire roof can be enclosed and the emissions evacuated as an alternative to a hood or a dog-house [EIB, 2012].

Especially in the beginning, during the loading and the first stage of the smelting process when the furnace is open or partially open, vapours and dust are created. The quantity and composition of these depend to a large extent on how clean the scrap is. Scrap from wrecked cars, household appliances or beverage cans, for example, contains coatings that consist largely of organic binding agents but also contain metallic pigments. These coatings will (especially at the start of the smelting process) be only partly burned away and result in the formation of smoke and dust.

In considering the nature and quantities of the emissions, the different sources of dust and fume emissions, as described above, demonstrate that large differences exist between foundries, depending on the cleanliness of the charged material, the applied charging procedure, the composition of the charge, the refining treatments and on the additions to the melt. Since no coal or fuel is burned in steel foundries the furnace the emissions solely depend on these parameters [EIB, 2022]. In (secondary) steel making fuel burners using natural gas and oil may be used to assist the early stages of melting and also carbon might be injected to allow the generation of a foamy slag EIB, 2012].
Both the BREF for smitheries and foundries [EIB, 2022] and the BREF for the iron and steel industry contain emissions factors for dust and the quantity of slag that is produced when smelt steel in electric arc furnaces. In foundries, the quantity of dust ranges from 5 to 8 kg per ton of metal (load). The resulting quantity of slag can vary widely depends on the type of lining and will be in the range of 10 to 40 kg per ton of metal for furnaces with an acidic (SiO) lining. The amount of slag produced will be twice as great when a furnace with a basic inner lining (made of MgO) is used. The amount of slag produced by EAFs in steelmaking is between 60 and 270 kg/t liquid steel. The wide range may have it's origins in the type of steel produced and differences in input material and plant characteristics. Clearly the amount of slag produced for foundries is in general smaller compared to steel

production. This is mainly due to the differences in the way EAFs are operated.

According to the BREF [EIB, 2012], for steel production in EAFs, the primary emissions are larger than the secondary emissions by a factor of 10. Also the amount of dust generated is highly variable between facilities ranging from 4 – 300 kg/t liquid steel. The total amount of dust generated in the flue gases is generally between 10 and 30 kg per ton of steel for 'regular' carbon and low-alloy steel (LAS/CS) and between 10 and 18 kg per ton of steel for high-alloy steel (HAS/SS). These numbers apply *before* any emission-control measures are taken; see Table 3.13 for an overview of the figures. The secondary emissions associated with loading tend to be in the range of 0,3 to 1 kg of dust per ton of molten steel; those associated with tapping are between 0.2 and 0.3 kg per ton of steel; and for leakages from the machinery, between 0,5 and 2 kg per ton of steel. The total for secondary emissions therefore results in 1.4 to 3 kg of dust per ton of steel. This is the quantity that is released without emission-reduction measures.

Table 3.12 Development of dust during the various production steps of smelting steel in electric arc furnaces, unabated emissions [EIB, 2012]

Source	Formation of dust (kg/ton steel)
Secondary emissions	
Loading	0.3–1.0
Tapping	0.2–0.3
Leakage	0.5–2.0
Total secondary	1.4–3.0
Primary emissions	
LAS/CS	8.6–27
HAS/SS	8.6–15
Total primary & secondary	
LAS/CS	10–30
HAS/SS	10–18

Generally the treatment of different off-gas flows (i.e. primary and secondary emissions) is performed in the same device, mostly in bag filters. Only in a few cases are ESPs and wet scrubbers applied [EIB, 2012]. Some 95% of the dust in the primary dust generated during the melting can be collected by direct extraction from a hole in the lid of the furnace [Rentz, 1997]. In combination with a hood over the furnace the collection of the primary emissions is improved to 98%. This would mean that about 60% of the remaining primary dust (5%) is collected by the hood. This seems to be in line with the capture efficiencies for secondary emissions at BOFs. This would mean that the total capture efficiency with 60% of the secondary emissions captured is about 94% (highest efficiency based on the average value of the ranges presented in Table 3.12). EIB [2012] states that 85 – 90% of the total emissions during a complete cycle tap-to-tap can be collected. Instead of applying a hood, the furnace can be encapsulated by a dog-house with similar or slightly higher collection efficiencies to the direct hole extraction-hood combination. According to EIB[2012] in some plants, for instance in

Japan, the entire roof is enclosed and the emissions are evacuated achieving a capture efficiency of 100%.

According to EIB [2012], emissions of chromium into air are extremely variable. Following the application of emission-reduction measures, chromium emissions range from 0.012 and 2.8 g per ton of molten steel. EIB [2022] also states that a portion of the chromium in dust and slag can occur in the form of chromium(VI). It is not specified to what degree chromium(VI) is present. The extreme variance in emission factors is a result of the major differences in the degree to which the emissions created can be captured and the collection efficiency achieved by the installed devices in practice. Emissions are also influenced by differences in the composition of the feed stock: chromium emissions are generally higher during the production of stainless steel. Another factor at play is which process steps are being carried out, for instance the blowing-in of oxygen and the addition of aggregates to make the desired adjustments to the composition of the load. According to EIB [2012], the total emission of dust to air varies from 4 to 300 g per ton of steel, showing that the lowest value and the highest value differ by a factor of 75, while for chromium emissions this factor is much higher (233). Chromium emissions from the production of alloyed and stainless steel tend to be many times higher. As previously stated, this is due to the higher chromium content which is used as an alloying elements in these types of steel.

3.5.4.2 Induction furnaces

When clean scrap is processed in an induction furnace, the resulting fine dust consists mostly of iron oxides. The greatest emissions occur at the start-up of the furnace while containing a cold load and when contaminated scrap is added. Contaminants can include the following:
- Rust on the scrap
- Dirt
- Paint
- Oil, lubricants and metalworking fluids
- Zinc on galvanised iron
- Presence of non-ferrous alloys in the scrap, e.g. solder connections, bronze inserts

Nearly all scrap is contaminated to some degree. Circulation scrap and production scrap are relatively clean yet may contain lubricants and metalworking fluids. All other scrap will usually contain rust, paint, dirt and so on. The quantity and composition of dust emissions depend on the composition of the scrap used, the smelting method (cold start or continuous), how fast the load is melted and (as stated above) the purity of the scrap that was used. The first load of the day is usually a cold start with relatively high emissions.

Emissions, in other words, are largely determined by two factors: the degree to which the scrap is contaminated and the chemical reactions that take place at high temperatures when the metal melts, producing metallic vapours.

Emission data for different types of furnaces used in the production of cast iron showed that the emission factors for total dust and PM_{10} are

more than 10 times lower for induction furnaces than for EAFs and cupola furnaces the latter two having similar emissions strengths [Gschwandtner and Fairchild, 1990].

RTI International (2012) contains an overview of the emission factors for dust for various types of furnaces, with a distinction being made between controlled and uncontrolled emissions and different types of capturing techniques. Besides the electric arc furnace and induction furnace, the cupola furnace has been included in the overview as well. The data shows that the emission factor of a single type of furnace can vary by as much as a factor of 10 when combined with certain emission-reduction techniques. The uncontrolled emission of dust for cupola furnaces is 7.4 kg (16.3 lb) per ton; for EAFs, this is 6.9 kg (15.2 lb) per ton; and for induction furnaces, this is 0.6 kg (1.4 lb) per ton. These figures are the calculated averages of the values reported in the various sources. The average emission factors for uncontrolled emissions from cupola furnaces and EAFs are comparable, while the emission factor for induction furnaces is 10 times lower.

When induction furnaces are used in the foundry industry, the BREF [EIB, 2022] states that the dust emissions are between 0.06 and 1 kg per ton of metal charge and the quantity of slag produced is between 10 and 20 kg per ton of metal charge. These figures apply to the smelting of both steel and cast iron.

The draft BREF for smitheries and foundries [EIB, 2022] contains more detailed information on emissions of specific elements to air. However, the multiple graphs included in the draft – which show the emissions of dust and chromium for each type of furnace – are illegible. It is therefore not possible to present the detailed data from that document here.

3.5.4.3 Measures for reducing emissions
For EAFs the treatment of different off-gas flows (i.e. primary and secondary emissions) is generally performed in the same device, mostly in bag filters [EIB, 2005 and 2012]. Only in a few cases are ESPs and wet scrubbers applied [EIB, 2012]. For induction furnaces is seems to be common to have bag filter in place. Best available technologies for steel foundries are cyclones and fabric filters [EIB, 2022]. Therefore for the smitheries and foundries only these two techniques are considered relevant in practise.

Abatement techniques such as bag filters can reduce dust emission by as much as 99%. Data from a report by RTI International [2012] show that fabric filters are more efficient for dust extraction than wet scrubbers. Fabric filters are generally highly efficient in removing both fine and coarser fractions of dust, while the wet scrubbers are less efficient, particularly for the finer fractions. A global indication of the capture efficiencies is given in Tabel 3.13, with the lower limit being applicable to the fraction of dust particles smaller than 2.5 µm and the upper limit applying to the fraction larger than 6 µm.

Tabel 3.13 Efficiency of various techniques for collecting dust

Emission-control technique	Capture efficiency
Fabric filters	99–99.5%
Wet scrubber, high efficiency	90–95%
Venturi scrubber	90–99%
Electrostatic filter	95–99.5%
Cyclone	90->99%*

* according to EIB [2022].

3.5.4.4   Summary of emission data
Using the information presented with regard to the quantity of dust generated, the chromium content of that dust and the efficiency of the abatement techniques, emission factors for the emission of chromium to air have been calculated for both untreated emissions and emissions to air after abatement. For induction furnaces, however, no data is available on the chromium concentrations in the slag and dust. Based on the information on emission factors for chromium and dust for the melting of cast iron in induction furnaces from Gschwandtner and Fairchild [1990], it is possible to derive an indicative chromium content. From the average emission factor of 1.12 g of chromium per ton of steel (reported values of 1.3 – 2 g Cr_2O_3/ton) and the average emission factor of 107 g of dust per ton of steel (reported values of 31.2 – 182 g/ton), the chromium content is around 1%. This seems a bit on the high side because the chromium content of cast iron is generally fairly low, although there are certain forms of cast iron to which both nickel and chromium are added [Bennink-Ten Cate, 2022]. Table 3.14 provides an overview of the information collected.

Table 3.14 Emission factors of dust and chromium into air for smelting steel and cast iron in electric arc and induction furnaces

Process	Steel (continuous casting)		Smitheries and foundries	
Type of furnace	Electric arc furnace		Electric arc furnace	Induction furnace
Sub type	LAS/CS	HAS/SS	LAS/CS	Steel and cast iron
Quantity of slag (kg/ton load)#	60–270		Acidic: 10–40 Basic: 20–80	10–20
Untreated dust (kg/ton load) #	10–30 (20)	10–18 (14)	5–8 (6.5)	0.06–1 (0.6)
			LAS HAS	
Cr concentration in dust (%)@	0.35	6.7	0.35 6.7	≈1%
Chromium emissions (g/ton)				
Measured/reported	0.012–2.8			1.3; 2.0
Calculated				
Untreated	70.2	938	22.8 435.5	0.6–10
Treated				
Fabric filters, 99%	0.70	9.38	0.23 4.36	0.006–0.01
Electrostatic filters, 95%	3.50	46.9	n.r.	n.r.
Wet filtration, 90%	7.02	93.8	n.r..	n.r.

* estimated based on emission factors for dust and chromium for cast iron foundries. # for steel production the emission factors are in kg/ton of liquid steel. @: Cr concentration from Table 3.12. n.r.: not relevant

3.6 Conclusions regarding chromium in sources, products, emissions and residues

With regard to the primary steel production process applying basic oxygen furnaces, the calculated total quantity of chromium that ends up in steel through the raw materials will be around 130 mg per kg of steel. These values apply to a situation in which the removal of chromium through slag is taken into account. If no extraction through slag is assumed, the calculated chromium content will be approximately 330 mg per kg of steel. The major sources of chromium in steel are iron ore and scrap. According to the calculations, scrap accounts for approximately 75% of the chromium entering the process. This illustrates the importance of scrap quality in terms of how much chromium ends up in the finished steel. With regard to secondary steel production using EAFs the impact of scrap quality is probably even more evident because scrap is virtually the only material used and other raw materials, such as slag forming agents, are used in much smaller quantities. Induction furnaces are used by steel foundries and partly used steel scrap with very little use of slag forming agents. Here, the chromium input depends on the scrap quality used and the share of scrap used in the raw material input. No data on the quantity of chromium(VI) in the raw materials and scrap was found.

Regarding the estimated chromium content in the hot metal and steel produced in the integrated steel process, it can be concluded that the values calculated in this report fall within the range of values found in literature.

Concerning the chromium balance of the BOF process and steelmaking by EAFs the following can be concluded:
- Producing a closed chromium balance for the integrated steelmaking process from general publicly available data is rather complicated due to several factors:
  - The quantities of by-products produced and the chromium content in those by-products are highly variable.
  - Furthermore, there is considerable uncertainty in the amount of chromium removed by slag in the blast furnace and consequently the amount of chromium in the hot metal. Using the average of the higher level hot metal chromium contents presented in literature, the chromium input approximately balances the output.
  - In order to balance detailed information on the inflow and outflow, the quantities and concentrations at a specific production location need to be determined carefully to produce a closed chromium mass balance.
- Because there is not much variation in the chromium content in the slags produced (minimum 1% and maximum 2.5%) by EAFs, the imbalance seems to be caused by the amount of slag produced. The amount of slag produced is highly variable. On the other hand the chromium content in the steel scrap is highly variable and in general likely to be higher than the assumed 0.1%. Low steel scrap qualities may be more common in secondary steel making using electric arc furnaces.

In general, for all types of furnaces major differences can exist in the nature and quantity of emissions. The composition and quantity of emitted material depends on the amount of scrap used, the purity of that scrap, the loading procedure employed and the refining processes which are carried out. In principle, these factors also play a role in the BOF process, which also involves the use of scrap. Analysis of the emissions shows that for the foundries the quantity of dust generated by the use of induction ovens is 10 times lower than that generated by EAFs. Comparing the emissions from EAFs used in the production of steel and EAFs used in foundries show that the emissions from foundries on average are lower (factor of three). This is mainly due to difference in the way EAFs are operated. The amount of dust generated by the BOF process and EAFs applied in steel making are comparable. Besides the way of operation, atmospheric releases are determined by the type and number of measures taken and the capture efficiencies and the removal efficiencies of the abatement techniques in place. Therefore, atmospheric emissions may strongly differ from plant to plant. Focussing on the technology of the furnaces, induction furnaces generate smaller amounts of dust. This is due in part to the fact that the use of induction furnaces involves fewer operations, such as refining the smelt, but is also a result of the more enclosed nature of induction furnaces, which allows less dust to escape. Mainly the processes of loading scrap (EAF) or loading hot metal (BOF) are a critical steps with respect to air emissions.

Looking at the chromium emissions, the difference between the EAFs and the induction furnaces is smaller due to the higher (estimated) chromium content in dust when induction furnaces are used. The emission of chromium to air as a result of the BOF process is more or less comparable to that resulting from the use of induction furnaces. This is largely due to the lower chromium content of the dust. The chromium concentrations for dust found in the literature, however, are very uncertain (especially for induction furnaces) and show a wide range of values. When comparing the environmental impact of the various processes, a purer comparison is obtained by looking at the total dust emissions.

Scrap is used for the production of steel by means of the BOF process and when an EAF or induction furnace is used. In the production of primary steel by means of the BOF process, this scrap accounts for just under 20%, whereas when an EAF or induction furnace is used, the production is based almost entirely on the use of scrap.

With regard to the contamination of scrap with paint, it is important to know that smoke is formed during the steel production (during loading of scrap in the furnace and in particular when charging the hot metal) and this smoke consists of dust particles of partially combusted organic materials such as paint. Considering the temperature of the hot metal of about 1200 °C it can be expected that the majority of the organic material if not all, is burned off during the hot metal pouring phase and will be emitted via the flue gases in this phase. It is thus like that no or very little of the Cr(VI) in the paint will end up in the molten metal bath. The presence of unwanted elements in the captured dust is one of the reasons why, for the purpose of primary steel production, preferably clean scrap is used whenever possible so that the captured dust can be

reused as a raw material. The reason for reusing the dust generated is that it consists largely of iron oxides. The expectation is that dust formed during the start phase of the primary steelmaking process will be primarily captured by the secondary flue gas treatment system, and if in place the tertiary system as well.

The degree to which it is possible to capture dust depends strongly on the phase of the BOF steelmaking process in which the dust is formed. The capture efficiency of secondary dust – such as that formed during the loading of the scrap (24–64%) and the tapping of the molten steel and the slag (49–55%) – is the lowest. For secondary dust formed during hot metal charging the efficiency is higher (89-94%). For primary emissions formed during oxygen blowing the capture efficiency is 89 – 99%. The emissions during scrap loading and especially hot metal charging are the most relevant with regard to chromium emissions resulting from coatings present on the scrap. With respect to paint on scrap it is likely that the majority paint and the chromium is transferred to the dust that is generated during hot metal charging. If that is the case, 89-94% of these emissions can be captured by the dust collection equipment.

Thus, based on the data presented on the secondary emissions it seems reasonable to assume that about 90% of the generated dust containing chromium (VI) is collected and 10% is emitted indirectly via indoor air to outside air . Use of a supplemental tertiary capture system can reduce non captured secondary emissions by approximately 50%.

Answers to the research questions addressed in this section:
2. *What are the emissions of chromium(VI) (and potentially other relevant metals) into the air (and, where possible, those into water and in waste flows) from various types of steel plants (per ton of produced steel)?*

    The emissions of chromium(VI) are difficult to estimate. There is no emission data on chromium(VI) available with regard to primary and secondary steel production. Similarly, virtually no information is available regarding the presence of chromium(VI) in the dust that is formed and emitted. The BREF for the iron and steel industry does mention the possibility of chromium(VI) emissions. Yet no additional (quantitative) information is included.

    Emissions of chromium(VI) will primarily be released into the air compartment. Emission into water may also occur through wet flue gas scrubber techniques. Judging by the difference in concentrations between the dry dust and the captured sludge, the emissions to water appear to be limited.

    The emissions of chromium(VI) to air depend greatly on the degree to which the occurring dust emissions are limited by the downstream flue gas cleaning systems and by the scrap quality and the share of scrap in the raw material input.

For steel foundries, generally the quantity of dust generated by the use of induction ovens is 10 times lower than that generated by EAFs. Within the (secondary) steel production, the amounts of dust generated by EAFs and BOFs are comparable. The dust emission from EAFs used by foundries are about a factor of three lower compared to steelmaking. When we look at the chromium emissions, the difference between the EAFs and the induction furnaces is smaller due to the higher (estimated) chromium content in dust when induction furnaces are used. The emission of chromium to air as a result of the BOF process is more or less comparable to that resulting from the use of induction furnaces. This is largely due to the fact that, although the dust emissions in the BOF process are higher, chromium content of the dust generated by the BOF process compared to the induction furnaces is lower. The chromium concentrations for dust found in the literature, however show a wide range of values and are uncertain, especially for induction furnaces.

When comparing the environmental impact of the various processes, a more sound comparison is obtained by looking at the total dust emissions. It can be stated that, due to a) the nature and quantities of the emissions, b) the different sources of dust and fume emissions, large differences exist between steel production facilities and also between foundries. The difference depend on the content in the charged material, the operation procedures such as applied charging procedure, the refining treatments and on the additions to the melt and whether coal or fuel is burned in the furnace. Additionally some differences are caused by the design of the furnace. Overall, with additional abatement measures, differences in atmospheric emissions can partly be levelled.

Based on the BREF, emissions of chromium to air from the BOF process are in the range of 0.01 to 0.075 g per ton steel.

Chromium(VI) emissions originating from the coatings on scrap are expected to occur primarily during steelmaking when the scrap is charged into the furnace and when the hot metal is charged and poured on the scrap. Based on the description of how dust emissions are formed during steel production, the expectation is that the majority of that dust will end up in the flue gas and not in the molten steel bath. The degree to which the emitted chromium(VI) will be captured depends mostly on the efficiency of the secondary and potential tertiary flue gas treatment system. It is expected that it is possible to capture at least around 90% (secondary treatment) and up to 95% (secondary plus tertiary treatment) of those emissions in BOF-steelmaking.

3. *What is the range of the amount of chromium in the primary raw materials used (per ton of steel produced)?*
   With regard to the primary steel production process, the calculated total quantity of chromium that ends up in steel through the raw materials is estimated to be in the range of 80 to 240 mg per kg of steel. These values apply to a situation in which

the removal of chromium through slag is taken into account. It is assumed that 50% is removed via blast furnace slag and 55% is removed via slag in the BOF. If no removal through slag is assumed, the calculated chromium content will be approximately 330 mg per kg of steel. The major sources of chromium in steel are iron ore and scrap. Based on the concentration in in the inputs, scrap accounts for approximately 75% of the chromium entering the process. There is some uncertainty in the removal of chromium by blast furnace slag. Some data suggest that the removal is less, about 10%. In the secondary steel process, scrap accounts for virtually 100% of the presence of chromium.

5. *Where does the chromium from these sources end up? (flue gas treatment residues, emitted fine and other particulate matter, waste/drainage water, alloying with newly produced steel, and so on)*
   Approximately 50% of the chromium present in the raw materials will end up in the slag formed during the BOF process. The remaining portion will end up in the steel being produced. A relatively small quantity is present in the collected dust (less than 1%) and less than 0.1% is expected to be emitted into the air (see section 3.4.3 and Table 3.6. Usually collected dust are recycled back into the production process and should therefore not be considered as a loss. The total quantity of chromium emitted to air in the range of 10-75 grams of chromium per ton of steel produced. As mentioned before, there is some uncertainty in the degree of removal of chromium via slag in the blast furnace. There is one study suggesting little removal of about 10% via slag. Another source suggests 50% removal without any further evidence.

4 Conversion and formation of chromium(VI) during steel production

This section addresses the information found in the literature concerning the degree to which chromium is captured by means of slag in the BOF process and the possible formation of chromium(VI) in slag and dust. We explore the formation of slag and the oxidation of alloying elements in the BOF process (section 4.1). The methods used to quantify chromium(VI) in steel slag are explained (section 4.2) and measurements of chromium(VI) in steel slag are presented (section 4.3).

4.1 Slag formation and the oxidation of alloying elements

The concentration of (potentially undesirable) alloying elements, particularly silicon and carbon, in the produced steel can be lowered by oxidising those elements and extracting them through slag. To promote slag formation, aggregates are added (mainly limestone). When oxygen is added, the elements oxidise and are absorbed by the liquid slag formed during the production process. The degree to which the elements oxidise depends on the presence of reducing agents (such as carbon and carbon monoxide gas), the amount of oxygen added, the composition of the molten steel (iron, but also other elements like manganese and vanadium) and the temperature. This is further elaborated in the following paragraphs.

With regard to extracting elements from the molten steel, a distinction must be made between the production of 'regular' steel and stainless steel. When producing regular steel, the goal is often to employ slag formation to limit the concentrations of certain elements, whereas when producing stainless steel, the objective is instead to limit the loss of certain alloying elements (primarily nickel and chromium) as much as possible. These goals are reflected in the process conditions.
In the presence of oxygen, metallic elements can oxidise to form metal oxides. The degree to which this occurs depends on factors including the temperature and how 'noble' the metal in question is. Some metals oxidise more quickly than others. The presence of other metallic elements plays a role as well. In principle, the least noble metal will be the first to oxidise and the noblest metal will be the last. When oxygen is being blown in to reduce the concentrations of carbon and silicon, other (less-noble) elements like iron and chromium are oxidised as well, together with other elements present (such as manganese and lead). Because an element like copper is much nobler than these metals, it will not oxidise until all the other, less noble metals have oxidised. For this reason, it is impossible (or virtually so) to extract copper from molten steel.

Many metallic elements have multiple valencies. This means that a neutrally-charged metallic element can 'give away' one or more electrons and, in the process, become positively charged. Depending on the number of electrons lost, a metallic element can occur in different conditions known as oxidation states. Chromium is known to be able to

take on all possible valencies from 0 to 6. This means that, as a neutral metallic element, chromium can give away six electrons in its maximum oxidation state. A metal such as vanadium will also have numerous oxidation states, in this case 0 to 5. While trivalent chromium is most common in nature, bivalent and hexavalent chromium (chromium(VI))) may occur as well. These forms of chromium can therefore, in principle, be found in the smelt and ultimately in the resulting slag. In addition to the nobility of the metals, it is important to consider how reactive the different oxides formed from the various metals are in comparison with one another.

Chromium(VI) can be formed by the further oxidation of chromium oxides with a lower valency. A few examples of these reactions are:
- oxidation of tetravalent chromium into hexavalent chromium: $2CrO_2 + O_2 => 2CrO_3$;
- oxidation of trivalent chromium into tetravalent chromium: $2Cr_2O_3 + O_2 => 4CrO_2$

The comparative stability of the various metal oxides in relation to one another can be illustrated using an Ellingham diagram. This diagram is used to indicate the temperature at which various metals are stable and at which temperature they will undergo spontaneous oxidation. In the diagram, the Gibbs free energy of a chemical oxidation reaction is plotted out against the temperature. This shows which oxide is most stable at a given temperature; see Figure 4.1.
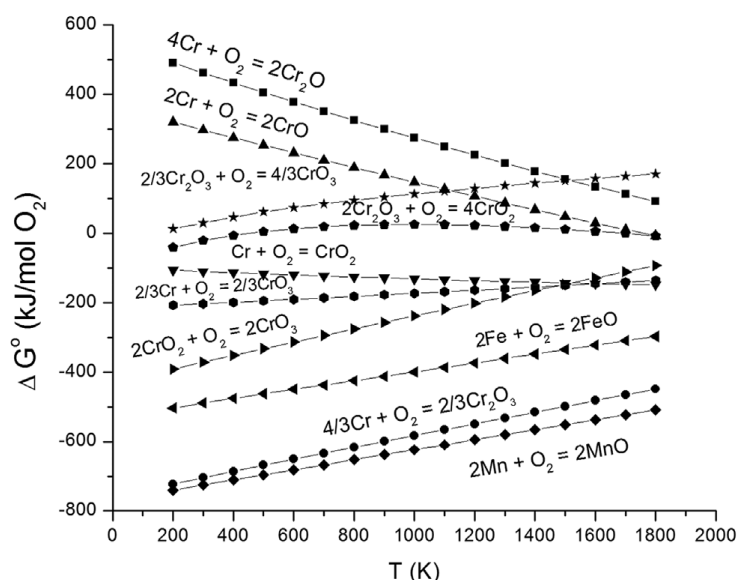
Figure 4.1 Ellingham diagram for various metal oxides. From Cheremisina and Schenk [2017].

The lines of dichromium trioxide (trivalent chromium) and manganese oxide are below those of iron oxide. This means that these oxides are formed more readily than iron oxide (FeO). The presence of a reduced metal such as iron will result in the reduction of an oxide if the Gibbs free energy for the formation reaction is higher than that of the metal itself. All oxides of chromium that are above the formation of iron oxide (FeO) will therefore be reduced by iron. However, beside the fact that

the oxides formed in the molten steel bath, it is also necessary to consider they are captured in the molten slag. Because this slag contains minerals, such as calcium, magnesium and silicon, the situation becomes much more complex. Chromium(VI) can actually be formed when slag cools under oxidising conditions [Cheremisina and Schenk, 2017]. The speed at which the slag cools also affects the degree to which chromium(VI) will be sequestered in certain (poorly) soluble mineral phases [Albertson, 2013]. Cheremisina and Schenk [2017] conducted thermodynamic calculations for different slag compositions that occur in practice and for different partial vapour pressures of oxygen. These calculations show that no mineral phases containing chromium(VI) are formed at any oxygen concentration.
However, numerous experimental and literature studies have demonstrated that chromium(VI) is being formed in slag in an oxidising atmosphere [Albertson, 2013, Sano, 2004 and Jahanshahi et al., 2004]. The BREF also mentions the potential presence of chromium(VI) in slag from the steel industry as an area for attention [EIB, 2022]. The basicity of the slag – i.e. the ratio of the sum of the quantity of (unbonded) calcium oxide and magnesium oxide to the quantity of silicon oxide – appears to be a strongly determinant factor. The higher the basicity, the more chromium(VI) is formed. Another important factor is the partial vapour pressure of oxygen: when this partial vapour pressure is higher, the oxygen concentration in the environment is higher and the formation of chromium(VI) will increase [Albertson, 2013, Bartie, 2004, Sano, 2004 and Jahanshahi et al., 2004]. Depending on the conditions, significant quantities of chromium(VI) may be formed in the slag, ranging from around 1% to over 20% of the total chromium concentration. Under certain circumstances, the ratio of chromium(VI) to total chromium may be as high as 60%, according to the model by Schwerdtfeger [Jahanshahi et al., 2004]. Figure 4.2 shows the results of this model, with the ratio of chromium(VI) to the total chromium content plotted against the partial vapour pressure for oxygen for two different types of slag with basicities (CaO/SiO_2 ratios) of 0.66 and 1.1. When the partial vapour pressure is 0.01 atmosphere or lower, the formation of chromium(VI) will be limited to a few percent or less.
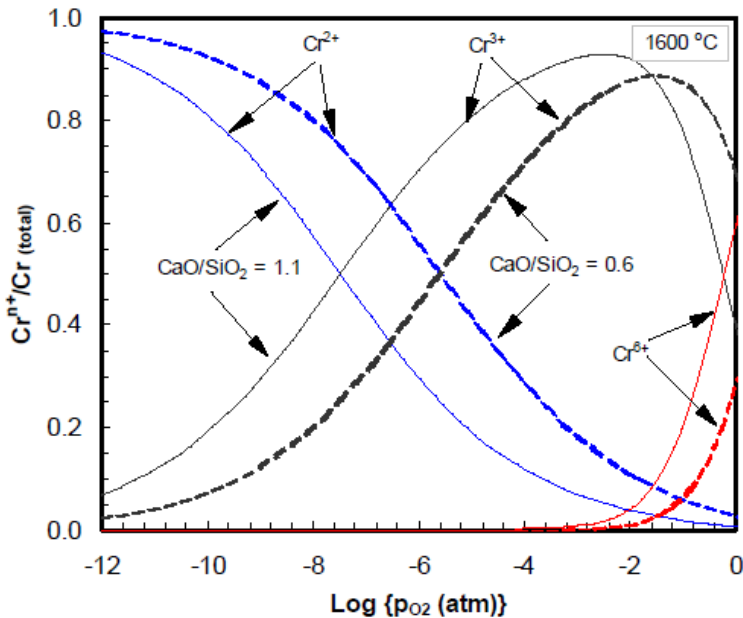
Figure 4.2 Ratio of chromium(VI) to total chromium (red lines) as a function of the partial vapour pressure of oxygen and the basicity of slag at 1,600 °C, according to the model by Schwerdtfeger [Jahanshahi et al., 2004].

4.2 Methods for measuring the chromium(VI) concentrations in slag and dust

Little information is available with regard to the chromium(VI) content of slag and dust resulting from steel production. In the studies we found, chromium(VI) is often measured using leaching tests conducted with captured dust or the slag. Leaching tests offer a means of investigating the environmental impact of a material. Such investigations are used to determine appropriate applications for a given material. The concentrations measured in the caustic solution cannot always be used to derive the actual total concentration in the original material because it is possible that a portion is not leachable (or only partly so) and will therefore not be rendered soluble. These measurement results provide an idea of only that portion which is readily leachable and therefore available. In addition, depending on the conditions during the leaching, chromium(VI) may be converted to trivalent chromium and vice versa (interconversion). To determine the total concentration of chromium(VI) in a steel-slag sample, it is necessary to use methods other than the leaching test. The methods in question are those where the chromium(VI) in the material is released entirely (or virtually entirely) and measures are taken to largely prevent the reduction of chromium(VI). However, interconversion remains an area of concern when using the available (standard) methods as well [Heringa and Janssen, 2018]. An example of such a method is described in Liu and Xue [2019]. A comparable European standard protocol which is applicable in the Netherlands for the analysis of chromium(VI) in solid materials (such as steel slag and dust) is NEN-EN-ISO 15192:2021. This standardardised method on analysis sets out a destruction involving the application of a highly alkaline solution.

DIN 19734 (1999) describes a method for determining the natural bioavailability of chromium(VI) in soil. Although originally intended for soil samples, this method can be used to ascertain whether slag meets the applicable environmental standards. The method therefore serves to establish the leachability of certain inorganic components. However, as will be further explained in a moment, this method is not suitable for determining the total chromium(VI) concentration because only the soluble fraction of chromium(VI) bonds will be rendered soluble. In the Netherlands, standard leaching tests have also been developed and validated for 14 heavy metals, including chromium in solid materials such as slag. These tests identify total concentrations in the leachate. The standard leaching tests are the column test (NEN 7373), the diffusion test (NEN 7375) and the shaking test (NEN-EN 12457-3). The statutory emission limit value for chromium, which can be identified using the aforementioned standard leaching tests, is based on total chromium and not chromium(VI). In other words, there is no specification/differentiation for chromium(VI).

In addition to these laboratory methods, it is also possible to apply methods for measuring in which the substance in question can be measured in the solid matrix and does not need to be released from the matrix through water extraction. With these methods, the problem of interconversion is not an issue. The chemical analysis of chromium and the different valencies of chromium found in solid materials such as slag can be conducted using X-ray spectrometry and various modified versions of that technique, such as:
   a) XRF: Wavelength Dispersive X-ray Fluorescence Spectrometry (WD-XRF) and Energy-Dispersive X-ray Fluorescence Spectrometry (ED-XRF);
   b) XRD: X-ray Diffraction Spectrometry;
   c) XPS: X-ray Photon Spectrometry.

XRF in particular is a very common and fairly easy to use analysis technique for quantifying the total concentration of elements such as chromium. An advantage of this method is that it allows you to identify nearly all elements in the periodic system with a single reading. As a result, XRF is also a valuable tool for identifying solid materials and clarifying their structure. To determine concentrations, it is necessary to first grind the sample into a powder in order to take the most precise measurements possible. Limits of detection as small as 0.1–1 ppm are possible. For the purpose of structure clarification, XRF is also employed in hybrid configurations, such as SEM-XRF (Scanning Electronic Microscope- X-ray Fluorescence Spectrometry).

XRD is an analysis technique that is especially well-suited to clarifying the structure of solid materials. The measurements take place on the surface of the sample material. Like XRF, this technique can be linked to an electron microscope to conduct SEM-XRD.

The XPS technique is used primarily for structural clarification. Using this method of analysis, it is possible to identify the atomic ratios and the different valencies per atom. As a result, we can calculate the proportions of the individual valencies (such as that for chromium, e.g. bivalent, trivalent and hexavalent chromium) as percentages of the total

amount of chromium. The total chromium content can be fairly accurately determined by means of an XRF analysis, so that the measurements obtained can then be used to derive the chromium(VI) concentration and the remaining valencies in the solid substance. In theory, it is also possible to measure chromium(VI) concentrations directly using XPS. To do so, it would be necessary to have a series of standard samples for which the chromium(VI) concentrations are known. The combination of XRF and XPS is an effective way to determine chromium(VI) concentrations in solid matrices.

4.3 Chromium(VI) concentrations measured in slag and dust

Table 4.1 contains the results of two publications (Liu and Xue, 2019; Ma et al., 2009). The chromium(VI) concentrations of two different samples (dust and slag) have been measured in two different ways (a total analysis based on destruction/extraction using a highly alkaline solution and a leaching test). Both materials sampled (dust and slag) were formed during the production of stainless steel and the total concentrations differed by a factor of two. The ratio of trivalent chromium (Cr^{3+}) to hexavalent chromium (Cr^{6+}) for both samples differed by a factor of six.

Table 4.1 Chromium(VI) concentration as compared to the total chromium content in slag and dust formed during the production of stainless steel

Product	Concentration (mg/kg)	Form of chromium	Method of measurement	Reference
EAF stainless steel dust	0.25	Cr^{6+}	Leaching test	Ma and Garbers-Craig et al. (2009)
	99.9	Cr_2O_3 as Cr^{3+}		
	400	Cr^{3+}/ Cr^{6+}		
	0.25%	Cr^{6+}/ Cr^{3+}		
EAF stainless steel slag	0.018	Cr^{6+}	Total analysis of original sample	Li and Xue (2019)
	43.52	Cr_2O_3 as Cr^{3+}		
	0.04%	Cr^{6+}/ Cr^{3+}		

The European standard protocol which is applicable in the Netherlands for the analysis of chromium(VI) in solid materials such as steel slag and dust is NEN-EN-ISO 15192:2021. This is similar to the method used by Li and Xue [2019]. When compared to the leachate test applied by Ma and Garbers-Craig, this protocol should offer a more accurate picture of the actual chromium(VI) content.

As part of a study into substances of very high concern in worked materials, waste flows and waste materials, Tata Steel and the waste-processing company Harsco commissioned SWECO to take measurements of the occurrence of chromium(VI) in different types of slag. An analysis report published by SWECO in 2020 lists the chromium(VI) concentrations measured in converter slag (LD steel slag), casting slag and ejected (slopped) slag [SWECO, 2020]. The samples were analysed in accordance with NEN-EN 15192:2006, which was the predecessor to NEN-EN-ISO 15192:2021.

Due to emerging doubts regarding the outcomes of this study on the part of Tata Steel and Harsco, the North Sea Canal Area Environmental Service (OD-NZKG) arranged for a follow-up study to be conducted by SGS [SGS, 2020] and their laboratory (SGS Institute Fresenius GmbH in Herten, Germany). A different method, DIN 19734 (1999), was used for the chemical analysis. This method of analysis involves extraction with a phosphate buffer in an acidic environment. This will not extract the total quantity of chromium(VI) compounds, but only the soluble fraction. This method is intended for use in determining the natural bioavailability of chromium(VI) in soil. The fraction of adsorbed and precipitated chromium(VI) compounds will therefore not be taken into account in the measured chromium(VI). Because the validity is based on soil matrices, this method of analysis is not necessarily suitable for other matrices of solid materials such as waste materials (e.g. slag). In addition, the limit of quantification is over two times higher than the limit of quantification established in the SWECO study: 1.0 mg/kg (dry matter) as opposed to 0.4 mg/kg (dry matter). The achievable limit of quantification for NEN-EN-ISO 15192:2021 is 0.1 mg/kg (dry matter). The results of both studies are shown in Table 4.2.

Table 4.2 Concentrations of chromium(VI) and total chromium in different types of slag

Slag	SWECO and Synlab (commissioned by Tata Steel/Harsco) mg/kg (dry matter)		Percentage of Cr-VI	SGS (commissioned by OD-NZKG) mg/kg (dry matter)
Method of analysis	NEN-EN 15192:2006			DIN 19734
	Cr-VI	Cr-total		Cr-VI
Converter slag, class 2	12	2000	0.6%	<1.0
Converter slag, class 3	7.9	2000	0.4%	<1.0
Casting slag	2.6	350	0.7%	-
Ejected slag	5.9	930	0.6%	<1.0
ROZA slag	<0.4	130	<0.3%	-
DAP casting slag	2.1	230	0.9%	-
Blast furnace slag	<0.4	46	<0.9%	-

Because DIN 19734 is not a suitable method for determining the chromium(VI) content of the slag, these results will be excluded from consideration in the further analysis. The chromium(VI) fraction of the total chromium content in the slag produced by Tata Steel varies from a maximum of 0.9% to less than 0.3%. The lowest concentrations were measured in blast furnace slag and ROZA slag. This is also in keeping with expectations, because the conditions in the blast furnaces promote reduction, meaning that the chromium oxides present will not (or virtually never) oxidise to form chromium(VI). Due in part to the high carbon content in the hot metal, this will not occur during the hot metal desulphurisation (ROZA) process either. The highest concentrations are found in converter slag.

If we look at *Figure 4.2*, the concentrations shown in Table 4.2 are in the area with partial vapour pressures for oxygen of between 0.0001 and 0.01 atmospheres. The ratios of chromium(VI) to the total chromium content are low in comparison to what could potentially be formed under the right conditions.

4.4 Conversion of chromium(VI) from coatings in the BOF process

Chromium may occur in steel slag in a variety of oxidation states and may originate from a variety of sources. This can be:

- chromium(VI) (and potentially trivalent chromium) present in paint layers on steel, which has entered the BOF process through steel scrap;
- chromium that has been added to steel as an alloying metal or chromium from chrome plated steel parts which in the waste phase, enters the BOF process through steel scrap. This usually pertains to metallic chromium;
- chromium as a trace constituent in aggregates (raw materials), where chromium usually occurs in the form of Cr(III).

During the BOF process, chromium that is present in the raw materials will undergo oxidation and reduction under dynamic and/or extreme conditions. the chromium will either make its way into the emitted dust and the steel slag being formed, or will remain in the molten steel as metallic chromium, Cr(III) or Cr(VI). Chromium(VI) is can expected to be mainly present in the slag and dust formed during oxygen blowen (primary dust).

In section 3, we stated that most of the chromium(VI) in coatings is expected to end up in secondary dust. It is difficult to indicate what will happen to the chromium(VI) in fully or partly combusted coatings. In order to determine what happens to the chromium(VI) in painted steel scrap, one important factor to consider is the composition of the dust. The composition of primary dust is expected to be comparable to that of the slag that has been formed. Secondary dust, on the other hand – particularly the fraction that is captured in the start-up phase of the BOF process – will have a different composition, which will depend greatly on the type of scrap used and especially on the degree to which that scrap is contaminated. The composition of that dust will not be comparable with that of the slag formed during the smelting and refining processes. Additionally, the conditions for chromium(VI) in the resulting dust also differ (in terms of temperature and oxygen content) from those in the molten steel bath. In the worst-case scenario, nothing will happen to the existing chromium(VI). This will presumably be the case in the event that reducing elements such as iron are absent in the dust formed during the start-up phase. Chromium(VI) that ends up in the molten steel bath and then in the slag will likely be partly reduced based on the ratio of chromium(VI) to total chromium in the slag. The proportion will depend to a large degree on the process conditions. Based on the measurement data presented for steel slag, that would mean that only 0.5% of the chromium(VI) present in the steel slag remains and the other 99.5% is reduced.

4.5 Conclusions

The conclusions below provide an answer to research question 6:
What is known about the formation and/or conversion of chromium(VI) during primary and secondary steel production?

The information found in the literature is ambiguous with regard to the potential formation of chromium(VI) in slag during the production of primary steel. We found a considerable number of studies that demonstrated the formation of chromium(VI) in slag. On the other hand, a fairly recent study [Cheremisina and Schenk, 2017] concluded – based on the theory of oxidation and reduction of metal oxides – that formation of chromium(VI) would not occur. Measurement data, however, shows that there is chromium(VI) present in the slag formed during the BOF process in an amount of around 0.5% of the total quantity of chromium. Little information is available on the chromium(VI) content in emitted dust. One study showed that, in dust, the fraction of chromium(VI) accounts for 0.25% of the total chromium (for dust formed during stainless steel production).

What happens to the chromium(VI) from the coatings during the BOF process depends on how it is released and where it ends up in the process. Chromium(VI) entering the process might end up in the dust formed during the process, the molten steel bath or the steel slag. The part that ends up in the dust being formed will probably not be reduced to trivalent chromium. It is expected that the larger part of the chromium(VI) present in the coatings will end up in the generated dust. A portion will end up in the slag and be mostly reduced, depending on the process conditions. The portion that ends up in the steel bath will likely be reduced in its entirety. Presumably, only a small part of the chromium(VI) will end up and remain as such in the slag or the steel. When quantifying the chromium(VI) in slag or process dust, it is essential that one applies the correct measurement methods. Chromium(VI) is difficult to measure. One reason for this is the need to ensure that the chromium(VI) present is not converted into other forms (oxidation states) of chromium during the process of taking and analysing samples. In principle, 'dry' methods of analysis – such as a combination of XRF and XPS – are most suitable for this.

5 Analysis of the potential relevance of chromium(VI) emissions

5.1 Assumptions for scenarios

Because measurements of chromium(VI) are lacking we defined scenarios to make an estimation of the relevance of these emissions. In this analysis, we use the available data to offer insight into the potential contribution of emissions from steel scrap with paint that contains chromium(VI), compared to the baseline emissions of chromium(VI) and total chromium from primary steel production (BOF-process). This provides an *indication* of the extent to which steel scrap that contains chromium(VI) can result in additional emissions of these metals. To that end, we compare a scenario in which no steel scrap contaminated with chromium(VI) is used in steel production to a scenario in which contaminated scrap is used. In the first case we presume that it cannot be ruled out that the total chromium emissions also contain chromium(VI).

Insight into the conversion of chromium(VI) to chromium(III) and total chromium content, and vice versa, is also vital in order to draw preliminary conclusions with regard to relevance. In order to analyse the potential relevance of chromium(VI) emissions based on the available data, we completed the four steps set out in this report:
1. Estimate of the quantity of chromium(VI) in contaminated steel scrap (from chapter 2).
2. Input and output of chromium(VI) and total chromium in the primary steel production process (from chapter 3 and 4).
3. Scenario analysis intended to gain insight into the relevance of chromium(VI) emissions originating from chromium(VI) containing paints which contain chromium(VI) (this chapter)
4. Conclusions

Because the emissions of chromium(VI) in primary steel production are unknown (only total chromium is known), we had to make an assumption regarding a reference emission of chromium(VI) in order to gain insight into the possible additional contribution of emissions from paint. With regard to total chromium, we estimated the mass flow involved in steel production. *Figure 3.4* provides an overview of the processes and estimates for the input and output per ton of steel for total chromium. Because chromium in metallic form is present in steel scrap and in the raw materials for steel production, also in the reference situation -to some extend- chromium can be converted into chromium(VI) during the production process and emitted.

We defined four scenarios (scenario A to D) to calculate the potential fraction of the total emissions of chromium(VI) that comes from chromium(VI) paints found in steel scrap. We varied two parameters with a lower and upper bound:
1. potential additional emission of chromium(VI) to air *coming from the chromium(VI) paint* in steel scrap (lower and upper level) and;

2. potential *reference emission of chromium(VI) to air* from steel production based on the proportion of amount of chromium(VI) to total amount of chromium in the steel slag (lower and upper level).

Combining the two sets of parameters (leading to scenario A, B, C and D) generates insight into the potential additional chromium(VI) emissions as a result of scrap with chromium(VI) from paints.

1. Scenarios for air-emission coming from paint.
Based on the available data on new paint layers, we have assumed that scrap from steel with a chromium(VI) containing coating has an average chromium(VI) content of 300 ppm (see section 2.3.6). If all scrap contains chromium(VI), the quantity that enters the BOF plant is estimated to be 57 g of chromium(VI) per ton of steel produced (190 kg*300 mg/kg= 57 g/ton), see Table 5.1. The average chromium(VI) content of 300 ppm, which is based on the calculated values of chromium(VI) in paint, is probably rather high considering the measured values in paint layer. Measured values are on average a factor of seven (three-ten) lower than the calculated values (see section 2.3.5).

Another important factor to account for is the percentage of steel scrap that contains chromium(VI) paints. The exact figures for this are unknown at this time. Based on an indicative estimate (see sub-section 2.5), about 2 percent of the scrap might contain chromium(VI) paint. Because this might be worst-case for the Dutch situation, we assume that 1% of the scrap is contaminated with Cr(VI), resulting is a Cr(VI) input of 0,57 g/ton.

Table 5.1 Chromium(VI) input from paint through steel scrap when producing 1,000 kg of steel in a BOF plant (see also Table 2.5)

	Amount of steel scrap	Cr(VI) content	Cr(VI) input	Cr(VI) emission to air lower bound	Cr(VI) emission to air upper bound
	(kg/ton steel)	(ppm, mg/kg)	(g/ton)	(mg/ton)	(mg/ton)
Average	**190**	**300**	**0.57**	**0,04**	**57**

Lower bound. In this scenario, it is assumed that chromium(VI) in the paints is emitted to the air from the steel furnaces similar to the emissions of total chromium. The input of chromium(VI) of (0.57 g/ton into the steelmaking process) is distributed over a) the emissions (0.01-0.075g total chromium/ton of steel, see Table 3.9), b) the produced steel and c) the slag, (see sub-section 3.4.3 and Table 3.6). The amount of chromium in the furnace can be calculated from the amount in slag, assuming that the amount in slag equals the amount in the molten metal (50% removal by slag). This results in a total amount of chromium in the BOF = 388.8/0.5= 778 g/ton. Alternatively, based on the average chromium content in crude steel of 243.5 ppm from the data reported by Persson (2019), the total amount of chromium in the BOF is 388.8 + 234.5 = 632 g/ton (see Table 5.2). The basic assumption in this scenario is that the emission factor for total chromium, ranging from 0.01-0.075 g/ton steel relates to the total

amount of chromium in the BOF. Based on the Cr(VI) input (0.57 g/ton), the total input of chromium in the BOF of 632 g/ton and the average emission factor of 0.043 g/ton (midpoint of the range of emission factors for total amount of chromium of 0.01 – 0.075 g/ton), a lower level emission factor of chromium(VI) to air through dust of *0.04 mg/ton* steel is calculated (0.57 / 632.3 x 0.043 x 1000 = 0.04 mg/ton). Conversion of Cr(VI) to other valences of chromium is not assumed.

Table 5.2 Quantity of chromium in steel and slag after treatment in the BOF plant and Cr-emissions to air per ton of produced steel (taken from Table 3.9).

Scrap scenario	Amount of Cr in slag (g/ton)	Total amount of Cr in the BOF (g/ton)	Emission to air (g/ton)
Average-case	389	778[a]/632[b]	0.01-0.075

a based on slag content and 50% removal by slag.
b based on content of chromium in slag and in crude steel.

Upper bound. In this scenario, it is assumed that 10% of the chromium(VI) present in the paint is released into the outside air along with the dust, diffusely and/or after air treatment (g/ton of produced steel). This is an order-of-magnitude estimate based on the capture efficiencies for hot metal charging mentioned in section 3.4.4.2. It is based on the range of 6-11% emission to outside air during the pouring of the hot metal on the steel scrap (capture efficiencies ranging from 89 – 94%). This step is expected to be the most important for emissions from paints. The remaining portion of the chromium(VI) (90%) is expected to be captured by the air treatment system. The assumption here is that all organic material on the scrap such as paints (included chromium(VI) is released during hot metal charging. Regarding the description of nature of the secondary emissions at BOF charging as provided section 3.4.4.2, 90% is thought to be a realistic value although higher efficiencies can be achieved (95%). Furthermore, air emissions from the BOF can further reduced by about 50% by tertiary systems. Thus the potential chromium(VI) emissions generated during hot metal charging may very well be a factor of four lower.

Assuming that 10 percent of the quantity of chromium(VI) that enters the BOF plant is emitted to indoor air, this leads to an emission of *57 mg/ton* steel. (10%*1%*190 kg*300 mg/kg; see Table 5.1).

2. Baseline Cr(VI)-emission-scenarios.The actual emissions of Cr(VI) are estimated because there are no data. The estimated potential quantities are reflected by the baseline scenarios and are based on the proportion of chromium(VI) content to total chromium content in the steel slag (lower and upper level).
Lower bound. Based on measurements, the ratio in slag is approximately 0.5% (see Table 4.2). Taking the total chromium emission to air emission of 10-75 mg per ton, this leads to a chromium(VI) air emission of 0.05-0.38 mg/ton of produced steel.

Upper bound. In this baseline scenario, the ratio of chromium(VI) to the total chromium content in slag is 10 times higher than the lower level baseline scenario: 5%. This value is set because the data suggest that in some processes and under certain conditions, the formation of

chromium(VI) in comparison with total chromium may be much higher (see section 4.1). This leads to a chromium(VI) air emission of 0.5-3.8 mg/ton of produced steel.

5.2 Results scenario's A, B, C and D

Because chromium in metallic form is present in steel scrap and in the raw materials for steel production, also in the reference situation -to some extend- chromium can be converted into chromium(VI) during the production process and emitted. In four scenarios (A, B, C and D), we indicate how much the emissions of chromium(VI) from paint could potentially add to the estimated baseline chromium(VI) emissions to air (in mg/ton of produced steel). The calculated ratios (see Table 5.3) give an indication of the range of the potential relevance of additional chromium(VI) emissions to air. This helps also to identify important factors that determine the relevance.

Scenario A. This scenario compares the emission situation assuming that the chromium(VI) from paint (coatings) will be distributed across the steel, slag and emissions to air in the same way as the total chromium (lower bound paint scenario), to the lower bound baseline emissions. The extra contribution from paint containing chromium(VI) is an increase by a factor 0.2 in comparison to the baseline emission (see).

Scenario B. Here we also take the lower bound paint scenario as in scenario A. However, we compare it to the higher bound baseline emissions. In this case there is a marginal increase (factor 0.02 higher) in chromium(VI) emissions due to steel scrap containing chromium(VI) paints.

Scenario C. Here we compared the upper bound paint scenario to the lower bound baseline emissions. The upper bound paint scenario assumes that 10% of the quantity of chromium(VI) in paint will be emitted to air. The underlying assumption is that all the chromium(VI) in paint is released from the scrap during scrap and hot metal charging and that 90% of the chromium(VI) released is captured by emission-control equipment. This comparison reveals that the chromium(VI) emissions might increase by a factor of 300 (100 to 1000).

Scenario D. The upper bound paint scenario is compared to the upper bound baseline emissions. From this comparison it appears that the chromium(VI) emissions might increase by a factor of 30 (10–100).

Table 5.3 Estimated chromium(VI) emissions to air for each scenario and the ratio of the chromium(VI) emission to air (two levels) originating from steel scrap with chromium(VI) paint, compared to the chromium(VI) emission to air without this steel scrap (two levels) (in mg/ton of produced steel). This calculation assumes that 1% of steel scrap contains coatings with chromium(VI).

Scenario	Air emission from paint (mg/ton produced steel)	Baseline air emission (mg/ton produced steel)	Ratio of Cr(VI) air emissions from steel scrap with CRVI paints to baseline air emissions
A. lower bound air emission from paint, lower bound baseline with ratio Cr-VI/Cr-total 0.5%	0.01-0.07	0.05-0.38	0.18
B. lower bound air emission from paint, upper bound baseline with ratio Cr-VI/Cr-total 5%	0.01-0.07	0.5-3.75	0.02
C. upper bound air emission from paint; lower bound baseline with ratio Cr-VI/Cr-total 0.5%	57	0.05-0.38	268 (152–1140)
D. upper bound air emission from paint; upper bound baseline ratio Cr-VI/Cr-total 5%	57	0.5-3.75	27 (15–114)

Conclusions of the analysis
- It is clear that chromium(VI) emissions are highly dependent on the assumptions of what precisely happens to the chromium(VI) origination from paints during the charging of steel scrap and the pouring of the hot metal on the steel scrap in the basic oxygen steel production process.
- When the chromium(VI) in paints behaves in the same way as the chromium that is present in molten steel, the emissions will increase by 2 – 20 percent. Emissions of chromium(VI) from primary steel production may be significantly higher compared to estimated regular chromium(VI) emissions when chromium(VI) that is present in paints is largely released during scrap charging and while the hot metal is poured on the steel scrap.
- Information concerning the portion of steel scrap that is contaminated with chromium(VI) is essential in order to draft realistic scenarios. Based on the rough estimate in sub-2.5 of 2% as an upper level, a level of 1% (thought to be more realistic) is used in the calculations.
- The assumed average Cr(VI) content of 300 ppm can be high considering the measured values in paint layers. On average these are a factor of seven lower than the calculated levels, but measured show a wide range of concentrations. Thus, based on measured Cr(VI) levels the estimated emissions for the paint scenarios can be lower.

- More information is needed concerning diffuse emissions during the process of loading steel scrap into the converter and charging the hot metal. It was assumed that 10% of all chromium(VI) present in the coatings will be emitted to air. The evaluation in chapter 3 (see sub-section 3.4.4.2) shows that 36 to 76% of the dust emissions likely containing chromium(VI) is released to the atmosphere during scrap charging (capture efficiencies range from 24 – 64%) and 6- 11% of these emissions is released when pouring the hot metal on the steel scrap (capture efficiencies ranging from 89 – 94%). The approximate contribution to the total emission to air for each of these two is unknown to us. However we expect that the majority of the emission of chromium(VI) that originates from the presence of paints, occurs when the hot metal is poured onto the scrap. If that's not case the emissions are likely to be even higher than the assumed value of 10%. When the capture efficiency is higher (95%) and a tertiary capture system is in place, the calculated emissions of chromium(VI) to air may be reduced by about a factor 4.

6   Conclusions and recommendations

This investigation focuses on the question of how potential emissions into the air of chromium(VI) resulting from the processing of steel scrap with paint containing chromium(VI) relate to the total emissions of chromium(VI) in connection with primary and other steel production. The investigation is based on the available data regarding the composition of steel scrap and regarding the composition of raw materials and products from primary and secondary steel production. The results from section 2 concerning the quantity of chromium(VI) in rust-resistant paints and scrap and section 3 on the total quantity of chromium from the raw materials that ends up in the final product (steel), are summarised in Table 6.1.

Table 6.1 Summary of the results concerning the chromium(VI) content of painted steel and the calculated chromium contents of hot metal and steel in connection with the integral blast furnace process

Product	Concentration (ppm)	
	Range	**Chosen value**
Chromium(VI) in primers	40,000–100,000	
Chromium(VI) in total paint layer,		
Calculated	7,000–20,000	
Measured	20–10,000	
Coated steel (Chromium(VI)),		
Calculated		
Sheet steel	200–900	500
Construction beams	<u>40–200</u>	<u>140</u>
Overall		300
Steel scrap (Cr-total)	70–3,400	1,000
Hot metal (Cr-total),		
Calculated	70–150	
Measured	90–360	235
Produced steel (Cr-total),		
Calculated	130–330	
Measured	210–280	

Chromium(VI) in paint and steel scrap (questions 1 and 4)

- Based on the literature and measured values, it is possible to make a good estimate of the expected quantities of chromium(VI) in paint layers. For steel scrap that has been treated with rust-resistant primers, there is greater uncertainty surrounding the estimate because the concentration will also depend on the weight and shape of the treated material.
- The average quantity of chromium(VI) measured in paint layers containing chromium(VI) seems to be somewhere between 1,000 and 3,000 mg per kg of dry paint. The total range varies from 20 to a maximum of 10,000 mg per kg of paint (Table 6.1).
- Based on the safety and technical data sheets for *primers* containing chromium(VI), the concentrations of chromium(VI) in both the primers and the total paint layers (including top coats)

have been calculated. The concentrations in the primer are in the region of 40,000 mg per kg of dry paint for zinc chromate and around 100,000 mg per kg of dry paint for strontium chromate. For the entire paint layer, the calculated concentrations range from around 7,000 to 20,000 mg per kg of paint.

- As a whole, the measured concentrations of chromium(VI) in paints (on average 2000ppm) are lower than the estimated concentrations in paints (on average a factor of seven). Several explanations are given for this observation.
- The estimated chromium(VI) content in *painted steel* for the entire object is highly dependent on the shape of the object (whether it is a sheet or a beam). The chromium(VI) content of painted (thin) sheet steel (200–900 ppm) is close to the expected average quantity of total chromium in scrap (1,000 ppm). For structural steel beams, the contribution is a factor of 5–10 lower compared to the indicative average total chromium content of 1,000 ppm.
- The total chromium content expected to be found in clean, well-sorted steel scrap with no stainless steel/alloys (1,000 ppm) is a factor of 3 higher than the average quantity of chromium(VI) in objects/equipment treated with chromium(VI) containing paint (300 ppm in sheets and beams; see Table 2.4).
- In terms of order of magnitude, steel itself is expected to contain an total amount of chromium (200 ppm) roughly equivalent to the amount of chromium(VI) in painted steel (300 ppm).

Emissions from chromium(VI) and total chromium (question 2)

- Based on the BREF document, the emission to air of chromium from the BOF process is 0.01–0.075 g per ton of produced steel. It is unknown what portion of this is chromium(VI). In a scenario analysis an estimation is given based on the presence of chromium(VI) in slag.
- Emissions of dust that occur during the use of induction furnaces are a factor of 10 lower than those associated with the use of EAFs and the BOF process. It is possible to greatly reduce the occurrence of emissions by means of primary, secondary and in some cases even tertiary vent systems. The final emissions will be determined by which treatment systems have been installed and their capture efficiency.

Chromium balance of the primary steel production (question 3)

- The investigation has yielded effective insight into the total chromium balance in primary and secondary steel production (see Table 6.1 for the balance for the integrated blast furnace process).
- Based on this investigation, it is evident that no emissions data or measurement data for chromium(VI) in steel production are available, except in relation to slag.
- Steel scrap contains around 10 times as much total chromium as crude iron and is the primary source of chromium in produced steel (see Table 3.1).
- The quantity of chromium which, is added to steel through the primary raw materials and scrap is between 130 and 330 mg per

ton of produced steel. The largest contribution comes from the iron ore (see Figure 3.4).

- Regarding the estimated chromium content in the hot metal and steel produced in the integrated steel process, it can be concluded that the values calculated in this report fall within the range of values found in literature.

Where does the chromium from the raw materials end up (question 5)?

(Destination/purpose and distribution)

- Approximately 50% of the chromium present in the raw materials will end up in the slag formed during the BOF-process. From the perspective of the chromium balance a relatively limited quantity is emitted to air. According to the BREF document, the emissions of chromium to air are highly variable, in the range of a 12 up to 2800 milligrams per ton of steel. The total quantity of chromium in dust generated is about 70 grams per ton of steel. Chromium present in the generated dust may end up in waste water when a wet flue gas filtration technique is used. For secondary emissions, generally dry techniques such as bag filters and dry ESP are used and for primary BOF gas dust is removed using venturi scrubber. Based on the small difference in chromium content between the dry dust and the collected sludge, the emissions through waste water are also expected to be rather small in the light of the chromium balance of the BOF.

Conclusion regarding the conversion of chromium(VI) to chromium(III)

and vice versa (question 6)

- Based on theoretical considerations, it does not seem possible for chromium(VI) to form from other oxides of chromium during the BOF process. However, measurements show that chromium(VI) is in fact formed in the slag that is produced during the production of steel. Recent measurements show that the quantity of chromium(VI) is limited relative to the total amount, around 0.5%. Under certain conditions, this can potentially be much higher – up to 50% of the total.

Main conclusion and uncertainties

- Based on the inventory, effective insight was gained into the input and output of total chromium in the primary steel production process. No data is available on the chromium(VI) content of the primary raw materials. Neither is there an expectation that chromium(VI) will be present in those materials.
- It is concluded that chromium(VI) emissions due to steel scrap with chromium(VI) are highly dependent on what exactly happens to the chromium(VI) in paints when the hot metal is added to the steel scrap in the primary steel production process. In the lower bound scenario, the additional emissions are expected to be in the same order of magnitude as the reference emissions. In the upper bound scenario in which emissions to air occur during the loading of scrap emissions of chromium(VI) from paint in primary steel production may be significantly higher (57mg Cr(VI)/ton steel) than in the baseline air emission (0,4-

4mg/ton steel). Based on measured Cr(VI) content in scrap with Cr(VI)-paints instead of calculated values, these levels can be lower than estimated. The measured concentrations show a wide variability.

- Diffuse indoor emissions during loading of the scrap might also lead to notable exposure of workers due to inhalation.
- The scenario's show that there is a high degree of uncertainty regarding the diffuse emissions during the process of loading steel scrap and hot metal into the converter. It is still unclear which portion of the chromium(VI) ends up in the bath and which portion ends up in the dust emissions. Considering the description of origins of fumes generated during charging it seems likely that largest fraction will be release with fumes and dusts generated while charging the hot metal on the scrap. There is a high potential of atmospheric release because the fraction of the dust that is not captured during this phase can vary from 6 to 11%(see sub-section 3.4). An additional tertiary capture system could reduce these emissions by about 50%. There is also some uncertainty about the conversion of chromium(VI) from paints to chromium(III) or metallic chromium. Because of these uncertainties the outcomes should be used with care.
- The potential diffuse indoor emissions of chromium(VI) during charging activities might also lead to exposure of workers.
- Information concerning the portion of steel scrap that is contaminated with chromium(VI) is essential in order to draft realistic scenarios. Based on the rough estimate in sub-section 2.5, first an uncertain portion of 2% was assumed. For various reasons, this figure is considered to be conservative and a value of 1% is used in the scenarios.
- The estimated emissions of total chromium from the BOF process are expected to be higher than those from the use of induction furnaces in the steel melting process (foundries). Without emission-control measures, the emissions to air may differ by a factor of 10. Chromium emissions are highly influenced by the scrap quality and the degree of emission control. With regard to secondary steel production using EAFs the impact of scrap quality is evident, because scrap is virtually the only material used and other raw materials, such as slag forming agents, are used in much smaller quantities. Induction furnaces used by steel foundries also partly utilise steel scrap with very little use of slag forming agents. Here, the need for high quality (clean) scrap is evident. Considering the emissions to air, induction furnaces are therefore expected to be less.

Recommendations

- We recommend conducting measurements to gain further insight into dust emissions and the presence of chromium in dust during the loading of scrap in the primary steel production process.
- Because the scrap loading and the pouring of the hot metal only happens within a limited time span (5-10 minutes), it is recommended to focus on collection of dust on these moments in the air near the process to be able to estimate relevance for workers exposure to chromium (VI).

- We also recommend to analyse the ratio between total chromium and chromium(VI) in captured dust. It is also recommended to measure the absolute chromium(VI)-content in the captured dust coming from the primary, and secondary abatement systems. This gives a first indication of the relevance environmental exposure.
- We recommend generating insight into the residual material flows in the Netherlands of steel that is suspected to contain chromium(VI) from paints. This could consist of an inventory conducted by the managers of suspect objects and equipment, such as TenneT, ProRail, Rijkswaterstaat, the Central Government Real Estate Agency, Dutch Railways, the Ministry of Defence and scrap processors.
- Additionally it would be relevant for the future scrap levels to perform a historical assessment on the use of primers with chromium(VI) in the Netherlands. This could give insight in where it might still be present.
- In addition an investigation is recommended on the transport (export) and destination of that steel scrap to get insight in the total amount and potential location of emissions. This should be done in cooperation with the 'Human Environment and Transport Inspectorate'.

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Appendix A measured concentrations of Cr(VI) in dust (in Dutch)

Tabel A.1 Gemeten blootstellingsconcentraties voor inhaleerbaar stof en chroom-6 en de daaruit berekende gehalte chroom-6 in het tijdens het slijpen afgevangen stof. De gemeten concentraties zijn overgenomen uit Tabel 6.1 uit Peters [2018].

Medewerker/positie	Concentratie inhaleerbaar stof (mg/m³)	Concentratie chroom-6 (µg/m³)	Gehalte (ppm)
Persoonsgebonden luchtmetingen			
PAS slijpen schuurschijf	20,52	52,1	2539
PAS slijpen afbraamschijf	4,35	13,7	3149
Stationaire luchtmetingen			
STAT slijpen schuurschijf, 2m	27,87	41,6	1493
STAT slijpen schuurschijf, 5m	4,01	0,80	200
STAT slijpen afbraamschijf, 2m	1,09	0,747	685
STAT slijpen afbraamschijf, 5m	0,84	< 0,323	< 385

Tabel A.2 Gemeten blootstellingsconcentraties voor inhaleerbaar stof en chroom-6 en de daaruit berekende gehalte chroom-6 in het tijdens het schuren afgevangen stof. De gemeten concentraties zijn overgenomen uit Tabel 6.7 uit Peters [2018].

Medewerker/positie	Concentratie inhaleerbaar stof (mg/m³)	Concentratie chroom-6 (µg/m³)	Gehalte (ppm)
Persoonsgebonden luchtmetingen			
PAS schuren achterzijde	52,20	18,3	351
PAS schuren voorzijde	17,40	25,5	1466
Stationaire luchtmetingen			
STAT schuren achterzijde, 2m	0,61	1,92	3148
STAT schuren achterzijde, 4m	0,21	0,906	4314
STAT schuren voorzijde, 2m	0,22	0,926	4209
STAT schuren voorzijde, 4m	0,55	3,56	6473

Appendix B Chromium in raw materials (in Dutch)

B.1 Chroom in grondstoffen voor de productie van ruwstaal

B.1.1 Chroom in steenkool en kooks

Er kunnen vier hoofdsoorten kool worden onderscheiden: Antraciet, bitumineus, sub-bitumineus en bruinkool. Bij de productie van ijzer wordt een mengsel van verschillende soorten kool van verschillende herkomst gebruikt om er kooks (alternatieve spelling cokes) van te maken. Deze kolen worden ook wel metallurgische kolen genoemd. Meestal wordt gebruik gemaakt van bitumineus en sub-bitumineus kool [Metallurgical coal, 2022 en Corus, 2006] en soms antraciet. Bruinkool wordt niet gebruikt in de metaalindustrie voor de productie van metallurgisch kooks omdat het niet over de juiste eigenschappen beschikt. Van belang bij de selectie is de mate waarin de kolen geschikt zijn om kooks te vormen. Bepalend zijn o.a. de mate waarin de kolen vervloeien tijdens verhitting en het gehalte aan vluchtige bestanddelen. Het gehalte aan metaal elementen in kolen kan sterk variëren per soort, per regio maar zelfs binnen een kolenmijn in zowel laterale als verticale richting [Clarke en Sloss, 1992]. Zware metalen die aanwezig zijn in kolen zijn doorgaans gebonden aan de minerale fractie en niet aan het organisch materiaal.

De hierna genoemde concentraties hebben voor het merendeel betrekking op bitumineus en sub-bitumineus kool. Niet in alle rapportages is duidelijk om welke typen kool het gaat of wordt er geen onderscheid gemaakt naar type kool. De in de literatuur gevonden gehalten zijn totale gehalten aan chroom weergegeven als elementair chroom. De gehalten worden meest of weergegeven als totaal elementair chroom maar soms ook als chroom(III)oxides (Cr_2O_3). Typische concentraties van chroom in kool liggen in de range van 0,5 tot 60 ppm volgens een studie van de International Energy Agency (IEA) [Clarke en Sloss, 1992]. In hetzelfde rapport worden nog enkele specifieke studies aangehaald waarin het gehalte chroom is gemeten in bitumineus kool uit verschillende continenten:
- Australië: 5,95ppm;
- Mengsel 50% Oosten VS en 50% Polen 23,8 ppm;
- Oosten VS 1: 25 ppm en monster 2 18,3 ppm.

Daarnaast worden nog gehalten vermeld van bitumineuze kolen uit Ilinois: 14,1 ppm en Pittsburg: 14,5 ppm.

In een studie naar de emissies van zware metalen tijdens de productie van kooks zijn de gehalten zowel in de gebruikte kolen als in de geproduceerde kooks bepaald [Mu et al. 2012]. Het chroomgehalte in de kolen was 9,81 ppm (µg/g). In de geproduceerde kooks was gemiddeld nog 3,42 ppm aanwezig. Tijdens het productieproces is dus circa 65% van het chroom verwijderd via bijvoorbeeld het bluswater of via de afgassen (vliegassen).

Het gemiddelde gehalte aan chroom in bijna 8000 monsters van kolen uit de VS is 15 ppm [Finkelman, 1999]. In de betreffende publicatie is

geen onderscheid gemaakt naar de verschillende typen kool. Steenkool uit bepaalde regio's in China bevat een relatief hoog gehalte aan chroom, gemiddeld zo'n 300 ppm. Het gemiddelde gehalte in kolen uit China en voor de wereld is volgens deze publicatie respectievelijk 16 en 15,4 ppm [Cui et al. 2019]. In het rapport van Nalbandian [2012] wordt een gemiddelde chroomgehalte in kolen uit de VS vermeld van 20 ppm met een ondergrens van 0,5 en een bovengrens van 60 ppm, zie ook de gehalten vermeld in [Clarke and Sloss, 1992]. In het artikel van Lau et al. [2021] over emissies van sporenelementen tijdens het sinteren van ijzererts wordt een gemiddeld gehalte van 33,6 ppm vermeld met een minimum van 6,7 ppm en een maximum gehalte van 394 ppm.

De spreiding in het gehalte chroom in kolen is groot, variërend van minimaal 0,5 tot maximaal ongeveer 400 ppm. Aan de hand van bovenstaande gegevens is voor kolen die worden gebruikt voor de productie van kooks gekozen voor een gemiddeld gehalte van **20 ppm**. Voor de productie van 1000 kg kooks is 1220 tot 1350 kg kolen nodig [EIB 2012]. Tijdens het verhitten van de kolen worden vluchtige componenten afgedreven en ontstaan er kooksovengassen. Deze gassen worden eerst gekoeld en daarna ontdaan van nuttige producten zoals teer, ammoniak, zwavelzuur en een mengsel van benzeen, tolueen en xyleen (BTX). Uiteindelijk blijft gezuiverd kooksovengas over dat als brandstof kan worden ingezet. De zeer fijne fractie van het gevormde kooks wordt kooksbries genoemd. Deze kooksbries wordt weer bij de productie van sinter en pellets ingezet. Mu et al 2012 hebben de emissie van zware metalen tijdens de productie van kooks onderzocht. Het totale chroomgehalte in de gebruikte kolen was 9,81 ppm. Het geproduceerde kooks bevatte 3,42 ppm chroom. Tijdens het productieproces verdwijnt er dus ongeveer 65% chroom voornamelijk via de vliegassen en vermoedelijk door vervluchtiging tijdens het verkooksen van de steenkool. Wan et al. [2022] gaan uit van een verlies van 54% naar lucht. Uitgaande van 20 ppm chroom in steenkool en 65% verlies is het geschatte gehalte aan chroom in kooks 7 ppm. Kooksbries zou naar verwachting dezelfde concentratie aan chroom moeten bevatten als kooks. Echter, het chroomgehalte in kooksbries volgens Lau et al. [2021] is 148 ppm terwijl het geschatte gehalte aan chroom in kooks slechts 7 ppm is. Bij de berekening van de chroomtoevoer via grondstoffen aan het geproduceerde staal wordt voor kooksbries uitgegaan van het chroomgehalte volgens Lau et al. [2021]. Dit is vooral gedaan vanwege consistentie met de resultaten uit het onderzoek van Lau et al. [2021] voor sinter

B.1.2.   *Chroom in ijzererts*
Voor de inschatting van het chroomgehalte in ijzererts is gekeken naar de herkomst van het gebruikte erts. Wereldwijd gezien zijn Australië en Brazilië de twee grootste producerende en exporterende landen van ijzererts [USGS, 2021]. De grootste leverancier van ijzererts aan de EU is Brazilië gevolgd door Canada, Oekraïne en Zuid-Afrika. Deze vier landen leveren gezamenlijk zo'n 80% van alle ijzererts van buiten de EU [WITS, 2022a]. In de EU is Zweden de grootste leverancier van ijzererts met aandeel van ongeveer 7%. In 2002 werden door destijds nog Corus en momenteel Tata Steel hoofdzakelijk ertsen uit Brazilië, Zweden, Australië en Venezuela aangekocht [Corus, 2006]. In 2019 was de mix van geïmporteerd ijzererts anders met Canada als tweede en Zuid-Afrika

qua volume als derde leverancier en waarbij Australië en Venezuela uit de top vier zijn gevallen [WITS, 2022b].

Fanta en Op [2018] vermelden chroomgehalten in gangbare ertsen variërend van 0,9 tot 16,4 ppm. In een analyse naar de samenstelling van ijzererts uit de Sishen mijn in Zuid Afrika is het chroomgehalte bepaald op 0.01% (100 ppm) Cr_2O_3 wat overeenkomt met 68 ppm chroom [Williams, 2008]. Jacimovic et al. (2008) hebben de concentraties van sporenelementen in drie verschillende ijzeretsen gemeten. Voor het Australische erts was de chroomconcentratie 25 ppm, voor het Peruaanse 30 ppm en die voor erts afkomstig uit Zuid-Afrika 40 ppm. Het gemiddelde chroomgehalte in erts van een ijzerertsmijn en twee andere ijzerhoudende afzettingen in het zuiden van Brazilië is afgerond 58 ppm met een laagste waarde van 22 ppm en een maximum van 79 ppm [Spier et al. 2008]. De betreffende gehalten zijn gemiddelden van meerdere monsters. In Sweden wordt er in de streek Norbotten ijzererts gewonnen uit drie actieve mijnen te weten Kiruna, Malmberg en Svappavaara[LKAB, 2022]. IJzererten uit het noorden van Zweden (Tapuli afzetting) bevat gemiddeld 219 ppm Cr_2O_3 [Hasa, 2015], wat overeenkomt met 150 ppm chroom. Ertsen van het type Kiruna bevatten veel lagere gehalten aan chroom, < 10 ppm [Landergren, 1948].

In het artikel van Lau et al. [2021] worden verder nog chroomgehaltes van verschillende grondstoffen voor het sinterproces vermeld waaronder een gehalte in ijzererts van 45,08 ppm.

Voor de berekening van de totale input van chroom in de productie van ruwijzer zal worden uitgegaan van het chroomgehalte van **45 ppm** uit het artikel van Lau et al. [2021]. Gezien de in de literatuur gevonden gehalten voor ertsen afkomstig uit Brazilië, Zuid-Afrika, Sweden en Australië geeft dit getal globaal genomen een goed beeld van het te verwachten chroomgehalten in ijzererts.

B.1.3. *Chroom in sinter*

In van den Berg [2008] staan gehalten van Cr_2O_3 in sinter vermeld variërend van 0,019 tot 0,031% wat neer komt op Cr-gehalten van 130 tot 210 ppm. Lau et al. [2016] hebben een schatting gemaakt van het chroomgehalte in sinter op basis van de gebruikte grondstoffen en het de daarin aanwezige hoeveelheid chroom. Het berekende chroomgehalte is 104 ppm. Een belangrijke bijdrage leveren de residuen zoals slakken en afgevangen stof en slib uit het productieproces van staal. Het gehalte in deze residuen is volgens deze studie 220 ppm. Volgens Lau et al. [2016 en 2021] is het chroomgehalte in de interne retour van fijne deeltjes sinter (< 5mm) 83 ppm. Aan de hand van een massabalans van chroom voor het sinterproces is een inschatting worden gemaakt van het chroomgehalte in sinter. De hoeveelheden grondstoffen zijn gebaseerd op de BREF voor de productie van ijzer en staal [EIB, 2012] en voor de gehalten zijn de gegevens uit Lau et al. [2021] gebruikt.

Tabel B.1 Toevoer van chroom bij de productie van sinter. Benodigde hoeveelheid grondstoffen per 1000 kg sinter. Chroomgehalten afkomstig uit Lau et al. [2021].

Grondstoffen	Hoeveelheid grondstof (kg)	chroomgehalte (ppm)	Massa chroom (gram)
Kooksbries	45	148	6,6
Toeslagstoffen, flux	168	45,3	7,6
Retour fijne deeltjes sinter	251	83	20,8
Staalproductie residuen	159	220	35,0
IJzererts	813	45	36,7
Totaal	1436		106,6
Verlies via vrijgekomen stof			3,6
Totaal na verlies via stof			103,0

De voornaamste bijdrage aan de hoeveelheid chroom in sinter komt van ijzererts en via de gebruikte residuen uit de staalproductie. Kooksbries en andere toeslagstoffen leveren een beperktere bijdrage.

Uitleg verlies via stofemissies:

Een verliespost op de balans is de emissie van chroom via stofdeeltjes. Volgens Lau et al. [2021] ligt de emissiefactor van chroom voor lucht tussen 3,6 en 125,1 mg per ton sinter. De hoogte van de emissiefactor wordt voornamelijk bepaald door de efficiëntie van de emissiereducerende maatregelen. Afhankelijk van de toegepaste technieken ligt de efficiëntie tussen de 99,9 en 95%. Ervan uitgaande dat de laagste emissie factor geldt voor de emissiebeperkende techniek met de hoogste efficiëntie kan de totale hoeveelheid vrijgekomen stof en daarmee het verlies aan chroom in rekening worden gebracht. De hoeveelheid chroom in het afgevangen stof zou dan neerkomen op 3,6 mg gedeeld door (1- 0,999), wat gelijk is aan 3,6 gram chroom per ton sinter.

Het gehalte van chroom in sinter is ongeveer 107 ppm als ervan wordt uitgegaan dat er geen verlies van chroom optreedt in het productieproces. Wordt hier wel rekening mee gehouden, dan is het gehalte 103,0 ppm. Het berekende gehalte op basis van de gegevens van Lau et al. [2021] is dus lager dan de gehalten vermeld in van den Berg [2008] van gemiddeld 170 ppm en vergelijkbaar met wat Lau et al. [2016] hebben berekend. In deze RIVM studie wordt, voor de inschatting van de hoeveelheid chroom in staal, de berekende waarde zonder verlies naar lucht aangehouden.

B.1.4. **Chroom in pellets**
Voor de productie van pellets worden naast ijzererts, kookbries, kalksteen, kwartsiet en olivijn ingezet. Als bindmiddel wordt verder de kleisoort bentoniet gebruikt.

Voor de productie van pellets gebruikte Corus bentoniet afkomstig uit Griekenland en Sardinië (Corus, 2006). Bentoniet uit Milos, Griekenland bevat tussen <0.002 en 0.013% (<2-130 ppm) chroom [Olsson en Karnland, 2009]. Bentoniet uit Sardinië bevat circa 5 ppm chroom [Maccolo et al., 1999]. In de berekeningen wordt uitgegaan van bentoniet met een chroomgehalte van 5 ppm aannemende dat er vooral bentoniet met een laag chroomgehalte zoals dat uit Sardinië wordt gebruikt.

Keenfer et al. [2011] vermelden chroomconcentraties in olivijn van 0% en 0,01%. In Stopic et al. [2018] wordt een veel hoger gehalte vermeld van 0,45%. Voor het opstellen van de chroombalans wordt uitgegaan van een gehalte van 0,05% Cr_2O_3 [Huang et al., 2015 en Xi et al., 2001] oftewel 340 ppm chroom.
In Salminen et al. [2005] wordt een gehalte van 11 ppm chroom in kalksteen vermeld.

Volgens een onderzoek naar de samenstelling van kwartsiet gesteente uit Polen blijkt het gehalte Cr_2O_3 0,04% te zijn. Dit komt overeen met 272 ppm [Marciniszyn, 2013]. Het chroomgehalte in zeven kwartsietmonsters uit het oosten van India ligt in de range van 8,75 tot 181,6 ppm [Chaudhary and Alvi 2021]. Dit laat zien dat de chroomgehalten in kwartsiet aanzienlijk kunnen verschillen. Voor de chroombalans is uitgaan van een relatief hoog gehalte van 200 ppm. Bij de keuze is het gehalte in het Poolse kwartsiet leidend geweest. Onderstaande Tabel B.2 geeft naast de hoeveelheid grondstoffen die benodigd zijn voor de productie van 1000 kg pellets, per grondstof de chroomgehalten en daarnaast de hoeveelheid chroom in de grondstoffen die voor de productie van pellets worden gebruikt.

Tabel B.2 Hoeveelheid chroom in grondstoffen voor de productie van 1000 kg pellets.

Grondstof	Hoeveelheid grondstof (kg)	chroomgehalte (ppm)	Massa chroom (gram)
Kooksbries	12	148	1,78
IJzererts	952	45,1	42,91
Olivijn	28	340	9,38
Kalksteen	5	11	0,06
Bentoniet	5	5	0,03
Kwartsiet	10	200	2,00
Totaal	1002		56,16

De hoeveelheid grondstoffen die benodigd zijn voor de productie van 1000 kg pellets zijn gebaseerd op de gegevens uit de BREF voor de ijzer- en staalindustrie [EIB, 2012]. Als er geen verliezen optreden dan is de hoeveelheid chroom in 1000 kg geproduceerde pellets ongeveer 56 gram (56 ppm). De voornaamste input van chroom komt van het ijzererts (82%) en olivijn (15%) de andere grondstoffen leveren maar een beperkte bijdrage, zie tabel B.2.

Intermezzo:

Het negeren van verliezen is te rechtvaardigen als er overdracht plaatsvindt van chroom naar een andere medium via het gevormde product. Emissies van stof hoeven bijvoorbeeld niet meegenomen te worden als ervan mag worden uitgegaan de het stof ongeveer dezelfde samenstelling heeft als de geproduceerde pellets. Echter als er verdamping van metaaloxides tijdens het sinteren en het bakken van de pellets optreedt, dan moet dit verlies wel in rekening worden gebracht. Zo treden er aanzienlijke loodemissies op tijdens de productie van pellets o.a. doordat loodoxides verdampen, dat geldt in mindere mate ook voor chroomoxides [Lau et al. 2021 en Clark en Sloss, 1992].

B.1.5. *Chroom in ruwijzer uit de hoogovens*
Naast de pellets, sinter en ijzererts worden in het hoogovenproces kooks, injectiekolen, kwartsiet en ongebluste kalk toegevoegd. De hoeveelheid chroom in al deze grondstoffen is reeds in voorafgaande paragrafen aan bod gekomen.

Tabel B.3 geeft een overzicht van het chroomgehalte in alle grondstoffen, de hoeveelheid grondstoffen en de daaruit berekende hoeveelheid chroom voor het hoogovenproces. De data geven inzicht in de belangrijkste bronnen van chroom in ruwijzer en in de gevormde afvalstoffen. Alle hoeveelheden in Tabel B.3 hebben betrekking op de productie van 1000 kg ruwijzer.

Tabel B.3 Hoeveelheid chroom in grondstoffen voor de productie van 1000 kg ruwijzer.

Proces	Grondstof	Hoeveelheid (kg)	Cr-gehalte (ppm)	Massa Cr (mg)
Hoogovens	Pellets	352	56	19767
	Sinter	1120	107	119444
	Ertsbrokken	125	45	5635
	Kooks	355	7	2485
	Injectiekolen	152	20	3040
	Kwartsiet	11	200	2200
	Kalksteen	13	11	143
Totaal		**2128**	**96,9**	**152714**

De grootste toevoer van chroom komt voor rekening van sinter (78%) gevolgd door de pellets (13%). De overige grondstoffen dragen gezamenlijk zo'n 9% bij. Als de bijdragen worden betrokken op alle (primaire) grondstoffen inclusief die voor pellets en sinter dan is de procentuele bijdrage als volgt: IJzererts 40%; residuen uit de staal productie 26%; retour sinter 15%; Kooks incl. bries 7%; toeslagstoffen sinter 6%; olivijn 3%; injectiekolen 2%; kwartsiet 2% en bentoniet en ongebluste kalk samen minder dan 1%.

Zonder rekening te houden met verliezen komt het chroomgehalte in ruwijzer uit op 153 ppm. Dit komt redelijk goed overeen met het gemiddelde chroomgehalte in ruwijzer zoals vermeld in Wang et al. 2022] van 90 ppm. Volgens Corus [2006] komt ongeveer 50 -60% van

het in erts aanwezig chroom in de hoogovenslakken terecht. Uitgaande van 55% komt het chroomgehalte van ruwijzer ongeveer op 69 ppm. Hierop wordt verderop in dit rapport nog teruggekomen wanneer er nog naar de hoeveelheden geproduceerde slakken en stof wordt gekeken en de daarin aanwezige chroomgehalten en totale hoeveelheden chroom.

B.2 Chroom toevoer in de staalfabriek

Naast het ruwijzer, schroot en pellets worden kalksteen en gesinterde dolomiet ingezet bij de productie van staal in de oxystaalfabriek. Voordat het ruwijzer verder wordt verwerkt in de oxystaalfabriek, wordt het eerst nog ontzwaveld. Hierbij worden meestal magnesiumpoeder, calciumcarbide of ongebluste kalk toegevoegd.

B.2.1 Chroom in schroot

Voor de chroomgehalten in schroot, zie paragraaf 2.2. Voor de berekeningen wordt uitgegaan van een gehalte van 0,1% (1000 ppm) chroom.

B.2.2 Chroom in ruwijzer

Uit de chroombalans voor de hoogoven blijkt het chroomgehalte maximaal ongeveer 150 ppm (0.015%) en als er rekening wordt gehouden met het gedeeltelijk afvangen van het chroom in de slakken dan is het gehalte circa 70 ppm.

B.2.3. Chroom in toeslagstoffen

Voor het ontzwavelen wordt er uitgegaan van ongebluste kalk met eenzelfde chroomgehalte als kalksteen met een gehalte van 21 ppm chroom. Ongebluste kalk reageert met zwavel volgens de volgende reactievergelijking:

$$CaO + S <=> CaS + O$$
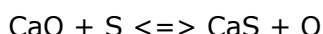
Tijdens het ontzwavelen wordt doorgaans 90% van het zwavel uit het ruwijzer verwijderd. Een deel van het zwavel verdwijnt via afgassen, via de slakken wordt circa 84% verwijderd. De totale hoeveelheid verwijderde zwavel is ongeveer 0,239 kg per ton ruwijzer [Schrama et al., 2017]. Volgens de bovenstaande reactievergelijking en het molecuulgewicht van de verbindingen kan de consumptie van CaO worden berekend: Voor de verwijdering van 1 kg S is 1.75 kg CaO nodig. Voor de verwijdering van de in het ruwijzer aanwezig zwavel via slakken is dan een hoeveelheid kalksteen nodig van circa 390 gram. De benodigde hoeveelheid kan in de praktijk echter sterk variëren van stoichiometrische verhoudingen tot een veelvoud (factor 5 of meer) daarvan maar soms ook lager. Op basis van gegevens voor het gebruik van magnesium tijdens het ontzwavelen blijkt de benodigde hoeveelheid magnesium in de praktijk gemiddeld een factor 1,5-2 hoger te liggen dan de onderlinge molecuulverhouding van de reactant en de gevormde stof (1:1) [Schrama et al., 2017]. De totale input van chroom is dan ongeveer 8,6 mg per ton staal. Dit is verwaarloosbaar ten opzichte van de andere grond- en toeslagstoffen en zal daarom verder niet worden meegenomen.

Behalve gesinterde dolomiet zijn alle overige grondstoffen al eerder aan bod gekomen. Gecalcineerde dolomiet uit het Zuiden van Polen heeft een chroomgehalte van 11 ppm [Gruszecka-Kosowska et al. 2015].

Appendix C Chromium(VI) content in slag and dust

Table C.1 Chromium content in slag, dust and sludge coming from various processes in the steel production

Slag

Process	Cr₂O₃-content (%)	Cr-content (%)	Reference
Blast Furnace	0.19	0,130	Kanel et al. (2016)
	< 0.01	< 0,007	Johnson (2017)
		0,002	Matthes et al. (2017)
		0,004	Ene and Pantelica (2010)
	< 0.1	< 0.007	Saqlain et al. (2018)
		0.002	Cabanova et al (2017)
		0.016	Cabanova et al (2017)
Desulphurisation	< 0.1	< 0.07	EC (2012)
	0.05	0.034	Schophuizen et al. (2018)
BOF-process	< 1	< 0.68	EC (2012)
	< 1	< 0.68	EC (2012)
	0.40	0.274	EC (2012)
	0.31	0.212	EC (2012)
	0.16	0.109	EC (2012)
	0.05	0.035	Tossavainen et al. 2007
	0.20	0.137	Yildirim and Prezzi 2011
	0.92	0.629	Radenovic et al 2013
		0.009	Ene and Pantelica (2010)
	1.25	0.855	Saqlain et al. (2018)
	0.45	0.308	Cheremisina en Schenk (2017)
		0.466	Cabanova et al (2017)
		0.480	Wunderlich et al.
		0.437	Spanka et al. 2018
		0.163	Spanka et al. 2018
		0.240	Chaurand et al. 2006
Secondary steelmaking	< 0.5	< 0.34	Rentz et al. 1997
	< 0.5	< 0.34	Rentz et al. 1997
		< 0.01	EIB 2012 (Tabel7.14)
		2.600	EIB 2012 (Tabel7.14)
	0.73	0.499	Kamseu et al. 2016
	0.27	0.185	Tossavainen et al. 2007
	0.37	0.253	Yildirim and Prezzi 2011
	0.92	0.629	Radenovic et al 2013
		0.001	Koleszár et al 2016

Process	Cr₂O₃-content (%)	Cr-content (%)	Reference
		0.008	Koleszár et al 2016
Secondary steelmaking	0.09	0.062	Cheremisina and Schenk (2017)
		0.001	Cabanova et al (2017)

Dust

Process	Cr₂O₃-content (%)	Cr-content (%)	Reference
Blast Furnace		0.085	Lau et al. 2021
		0.016	Stewart et al. (2022)
		<0.005	Stewart et al. (2022)
		<0.005	Stewart et al. (2022)
	0.11	0.075	Mombelli et al (2016)
	0.14	0.096	Mombelli et al (2016)
	0.18	0.123	Mombelli et al (2016)
		0.052	EC (2012)
		0.071	EC (2012)
BOF-process		0.018	Lau et al. 2021
		< 0.005	Stewart et al. (2022)
	0.05	0.034	Mombelli et al (2016)
		0.025	EC (2012)
		0.657	EC (2012)

Sludge

Process	Cr₂O₃-content (%)	Cr-content (%)	Reference
BOF-process	0.10	0.068	Omran en Fabritius (2017)
		0.006	Trinkel et al. (2016)
		0.007	Trinkel et al. (2016)
		0.007	Trinkel et al. (2016)

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