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RECOVERY OF CHROMIUM FROM STAINLESS STEEL SLAGS

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ABSTRACT

Residues from stainless steel production contain notable amounts of hazardous compounds such as chromium and other heavy metal compounds. These potential toxicity results in restrictions regarding the reusability of chromium containing slags, leading to landfilling instead of using them for other applications such as a substitution for natural aggregates in the construction industry. The paper shortly describes the physical recovery of the metals contained in the slag and its problems as well as the possibilities of a pyro-metallurgical reduction treatment. Different authors investigated possibilities to recover chromium from slags and treat the resulting slag with additives in order to improve their properties. Literature shows that it is important to optimize the process parameters to maximize the metal recovery rates and to influence the slags' leaching behaviour as well as its properties to get a marketable product.

INTRODUCTION

The stainless steel industry in western European countries produced 1.9 million tons of slag in 2012. [1] These slags contain heavy metal compounds such as chromium oxide that may be toxic, especially when chromium is oxidized to hexavalent chromium which is known to be a genotoxic carcinogen. This is why slags from the production of high alloy steel grades generally end up in landfills. Literature describes possibilities to treat the slag in order to recover the chromium. One of these treatments solely includes physical processes including a mechanical classification of the slag followed by the removal of metallic parts based on differences regarding the density or magnetic properties of the metal and slag phase. Another possibility is represented by a pyro-metallurgical treatment process that includes the reduction of oxidic compounds such as chromium oxide to metals and the separation between the metal and slag phase caused by differences of their densities. Finally, the addition of slag forming agents in the liquid slag decrease its leachability and can finally lead to a marketable product.

PHYSICAL RECOVERY OF CHROMIUM FROM SLAGS

Physical recovery mainly includes two steps, the classification of the slag in order to classify metallic parts, followed by the separation based on different physical properties of the slag and metal particles. The separation step can include centrifugation, sedimentation as well as gravity separation and magnetic separation. Literature reports that magnetic separation and gravity separation are already successfully implemented in commercial industrial scale processes [2]. However, the physical recovery of metals from the slag cannot recover oxidic compounds from the slag, which is why environmental problems are still present after the treatment. Another problem of this recovery process is the fine grain size of the resulting slag, what is leading to a hardly marketable product in western European countries. Therefore landfilling of these slags is still mandatory.

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NECESSARY PARAMETERS FOR CHROMIUM REDUCTION

The reduction treatment of slags requires optimized process parameters in order to achieve high recovery rates for chromium oxides. The most important parameters and their influence are summarized on the next pages.

Reducing Agent

Literature reports different applicable reducing agents to reduce chromium oxide, mainly carbon, silicon and aluminum. Figure 1 displays a Richardson diagram for selected compounds of stainless steel slags, calculated with thermodynamic data from HSC 8. It can be seen that from a thermodynamic point of view the reduction of chromium oxide is possible with manganese, silicon, aluminum and carbon at a temperature of more than 1200 °C. However, the Gibbs free energy difference of chromium oxide and manganese oxide are low and therefore it is not feasible to use manganese as a reduction agent. The advantage of aluminum is that the reduction results in the formation of Al_2O_3 which can build stable spinel type phases. The addition of silicon can positively influence the slags' properties, because the formation of SiO_2 decreases the basicity and therefore increases the volume stability of slags. However, metals are expensive reduction agent, which is why their implementation in an industrial scale process may be difficult. [3]

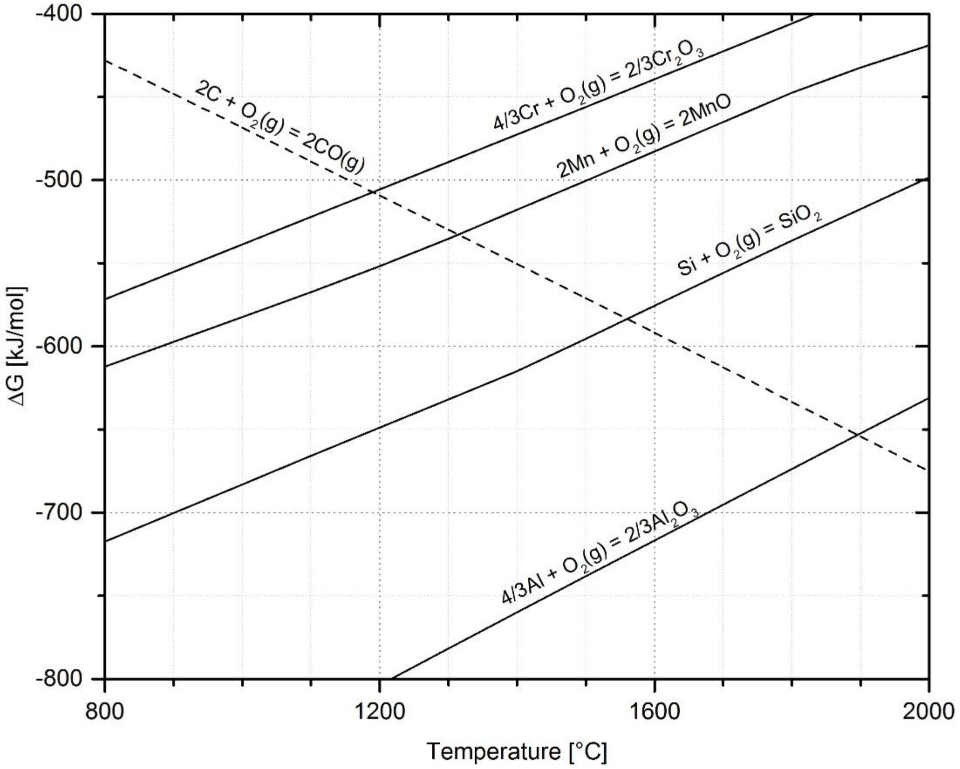

Figure 1: Richardson diagram for possible reducing agents of chromium oxide

Another thermodynamic calculation by HSC 8 can be seen in Figure 2. It shows the thermodynamic equilibrium of the reduction reaction in Equation 1 between chromium and chromium oxide, depending on the temperature and pressure. Carbides are excluded from calculations. The solid red line represents the equilibrium mass fraction of chromium oxide and the black solid line the equilibrium of chromium with an ambient pressure of 1 bar. The dashed lines show the same calculation with a decreased ambient pressure of 0.1 bar.

$$Cr_2O_3 + C \leftrightarrow 2Cr + 3CO(g) \qquad \text{Equation 1}$$

The calculation demonstrate that a temperature of about 1530 °C is necessary at a pressure of 1 bar in order to achieve a reduction degree of 95 %, as illustrated by the green line. When decreasing the pressure to 0.1 bar the same reduction degree is reachable with a decreased temperature of approximately 1320 °C. This is in agreement with Le Chatelier's principle. It is important to bear in mind that Figure 2 only describes the thermodynamic equilibriums and does not consider kinetic effects. However, it gives a good overview of the reachable chromium recovery rates.

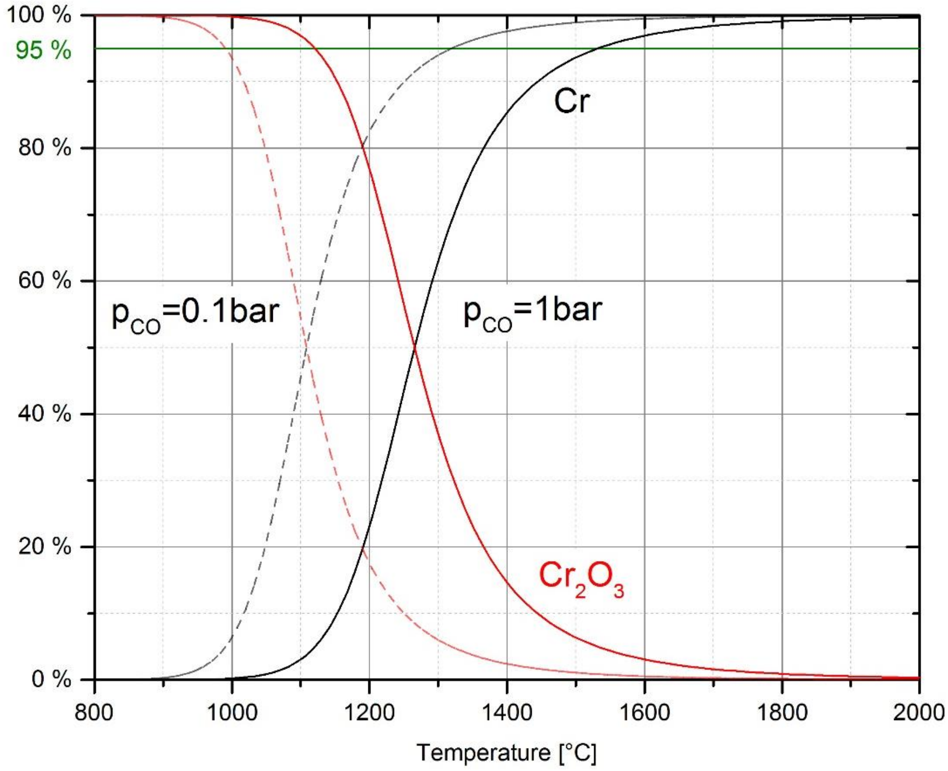

Figure 2: Thermodynamic calculations for the reduction of chromium oxide

Liquidus Temperature

A fully liquefied slag is of major importance for a pyro-metallurgical reduction treatment, because the occurrence of solid particles influence the process in a negative way. Chromium oxide can be enclosed within the solid particles and is then not accessible to the reduction agent. Furthermore, these particles decrease the reaction kinetics as well as the separation speed between the slag and the metal phase. Therefore, the process temperature must be higher than the liquidus temperature. Data to estimate the liquids temperature of slag system can be found in literature, for example in the "Slag Atlas". [4] Figure 3 displays the quaternary slag system of CaO-MgO-SiO_2-Al2O_3. The red dot references to the slag composition of Table 1, the yellow dot indicates a slag which is treated by the addition of 5 % SiO_2. In order to use a quaternary slag system, the slag composition for the four compounds have to be normalized. This leads to an increasing loss of accuracy with decreasing sum of the CaO, SiO_2, MgO and Al_2O_3. However, the obtained liquidus temperature from those slag systems gives a good understanding of how influence of adding slag forming additives on the process temperature.

Table 1: Typical chemical composition of a stainless steel slag [5]

	CaO	SiO_2	MgO	Al_2O_3	MnO	Cr
%-w.	43.3	29.7	8.6	10.1	1.9	2.4
%-w. + 5 % SiO_2	41.1	33.0	8.2	9.6	1.9	2.3

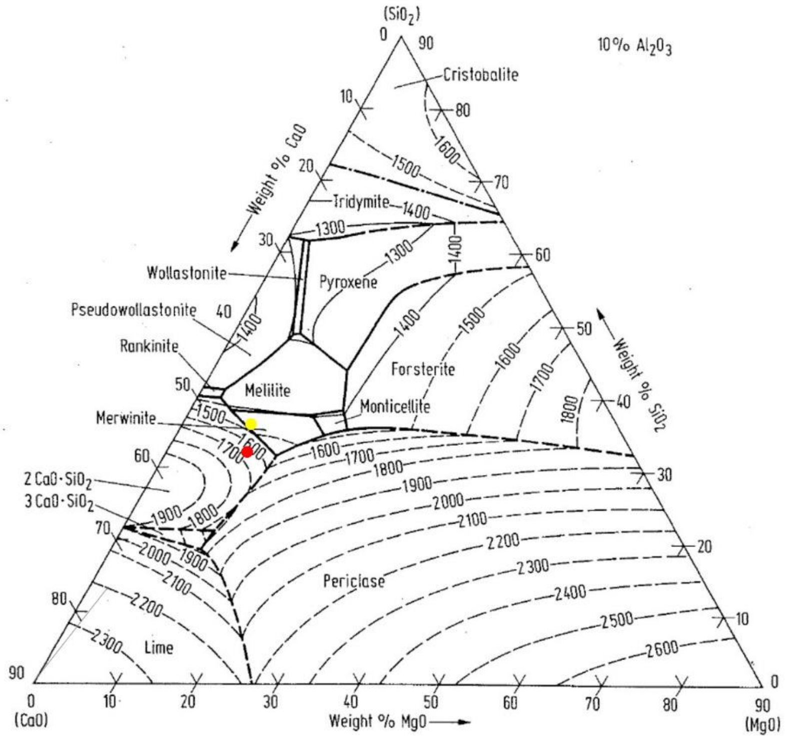

Figure 3: Quaternary slag system CaO-MgO-SiO_2-Al_2O_3 with a fixed Al_2O_3 concentration of 10%

Activity

The activity of a compound in the molten slag influences the reachable final concentration as well as the reaction kinetics. This can be explained by the influence of the activity coefficient on the chemical equilibrium. In general, an increasing oxide activity coefficient has the same effect as a higher oxide concentration and shift the equilibrium to lower oxide end concentrations. Equation 2 to Equation 4 illustrate this influence of the activity coefficient:

$$MeO + C \rightarrow Me + CO$$ Equation 2

$$K = \frac{a_{Me} \cdot p_{CO}}{a_{MeO}}$$ Equation 3

$$a_{MeO} = \gamma_{MeO} \cdot c_{MeO}$$ Equation 4

Chromium oxide in the molten slag is present in the oxidation stages Cr2+ and Cr3+. As can be seen in Figure 4, the fraction of Cr^{2+} depends on the total chromium concentration. At low chromium concentrations the main form of chromium oxide is CrO. With increasing chromium oxide content, the CrO fraction decreases and more Cr_2O_3 is present. The temperature slightly influences the oxidation state, so that lower temperature prefer the formation of Cr_2O_3. Literature shows that two parameters highly influence the activity of chromium oxide compounds: [6]

- the CaO/SiO_2 ratio and
- the temperature of the melt.

While an increasing CaO/SiO_2 ratio results in an increasing activity of the chromium oxides, higher temperatures decrease its activity coefficient. This fact can be seen in Figure 5.

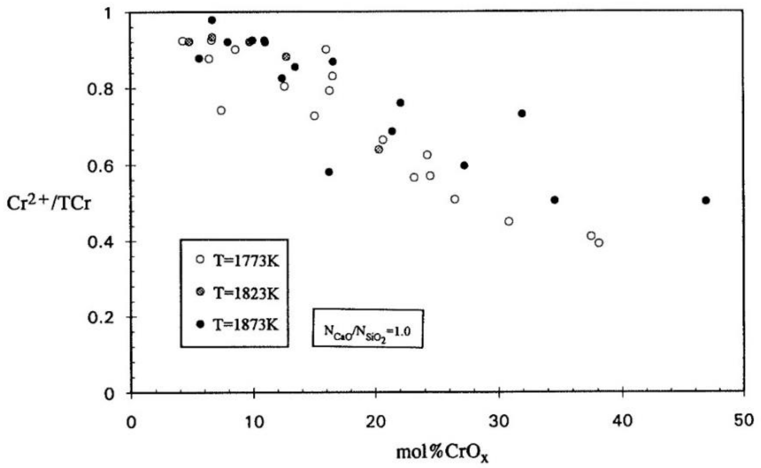

Figure 4: The effect of temperature and total chromium content on the oxidation state of chromium oxide

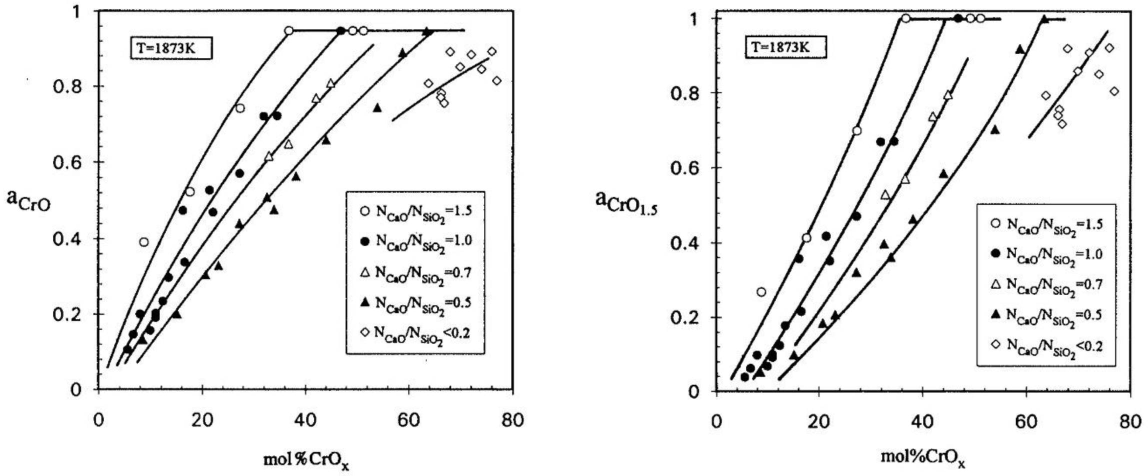

Figure 5: Influence of slag basicity on the activity at the temperature of 1873 K

Viscosity

A low viscosity is mandatory to ensure a fast separation between the metal and the slag phase. Different calculation models are available for the estimation of the viscosity of a slag system. One of those models is represented by the model of Urbain et al. [7]. Figure 6 illustrates the influence of the basicity on the viscosity of the slag displayed in Table 1. In order to lower the basicity, the slag composition was recalculated by mathematically adding SiO_2. It is important that Urbains' model does not consider the melting point of a slag system, which is why results around the liquidus temperature include some inaccuracies and should therefore be used with caution.

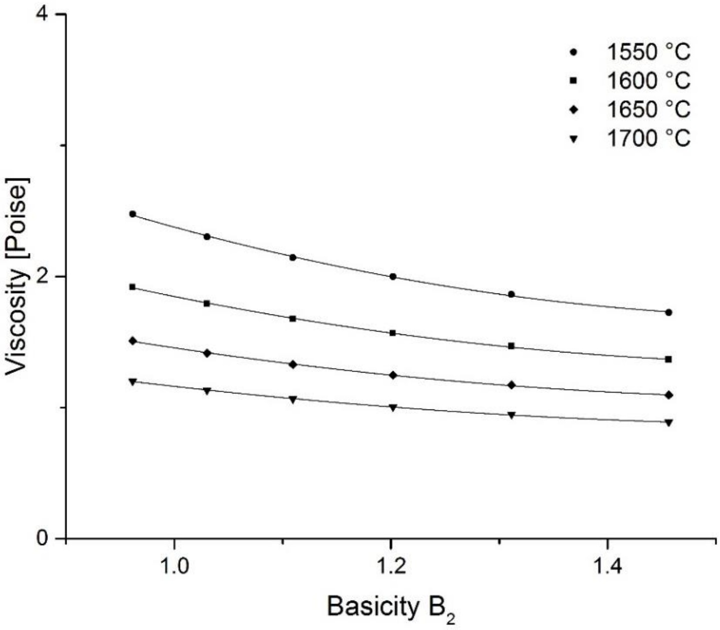

Figure 6: Influence of the basicity on the viscosity of slag systems

TECHNICAL PROPERTIES

Various authors showed that slags can substitute natural aggregates in the construction sector, especially as bituminous bound layers such as surface layers for road construction. Results obtained by the “Institut für Baustoffforschung” (FEhS) show that the technical properties of slags are comparable or even better than those of natural aggregates. However, it is important to control the content of free lime and free MgO in order to prevent the slag from hydration because this leads to a volume expansion which causes disintegration. Literature shows that a free lime content of less than 4 % is sufficient for most applications. One possibility that has already been tested in the steel shop of Thyssen Krupp Duisburg includes the tapping of the slag in a separate slag pot to ensure that the slag treatment has no influence on the steel quality. After tapping, the injection of dry sand and oxygen - as shown in Figure 7 - decreases the free lime content. The oxygen oxidizes metallic inclusions and iron(II)-oxide to iron(III)-oxide as can be seen in Equation 5 to Equation 7. This oxidation reactions generate heat which is necessary to dissolve the SiO_2 in the slag in order to form calcium silicates. The reachable free lime content is less than 1 % [5].

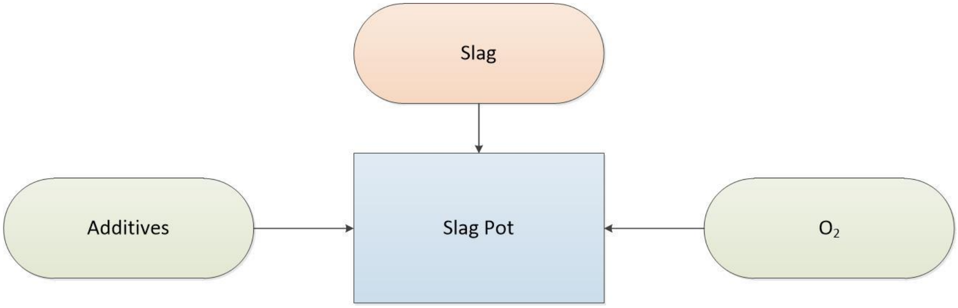

Figure 7: Injection of O_2 and sand

$$2FeO + O_2 \rightarrow Fe_2O_3 \qquad \text{Equation 5}$$

$$2CaO_{Frei} + SiO_2 \rightarrow 2CaO \cdot SiO_2 \qquad \text{Equation 6}$$

$$2CaO_{Frei} + Fe_2O_3 \rightarrow 2CaO \cdot Fe_2O_3 \qquad \text{Equation 7}$$

LEACHING BEHAVIOUR OF CHROMIUM FROM STAINLESS STEEL SLAG

In order to ensure harmlessness of slags regarding the environmental influence, the control of the leachability of heavy metals represents an important task, especially the leachability of chromium. Literature shows that the addition of different additives lead to the formation of stable and non-leachable chromium spinel compounds. The principal of such a stabilization process is the immobilization of toxic components contained in the slag, in order to reduce to prevent the environment from harmful influences. The leachability of chromium can be described with the so called “factor sp” and depends on the concentration of spinel forming agents in the slag. Equation 8 displays this empirical equation. The “n” represents a number between 1 and 4 and depends on the oxidation state of the iron oxide: [8]

$$0.2\,MgO + 1.0Al_2O_3 + nFeO_x - 0.5Cr_2O_3 \qquad \text{Equation 8}$$

The correlation between the “factor sp” and the leachability of chromium can be seen in Figure 8.

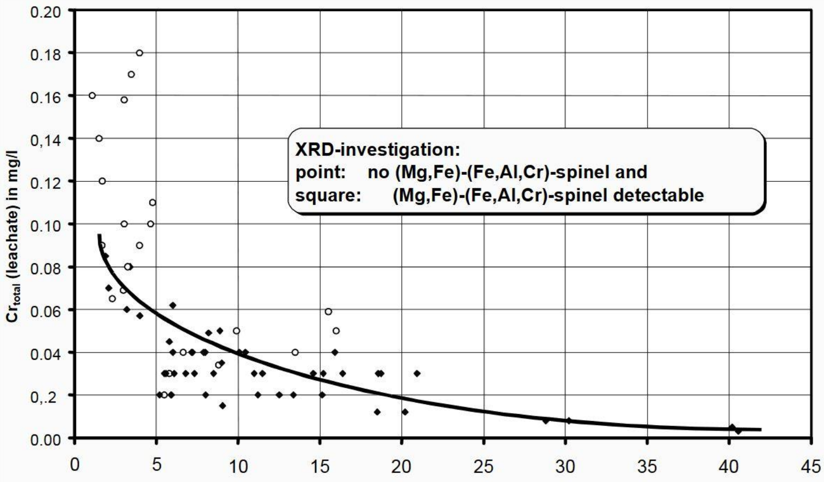

Figure 8: Influence of the "factor sp" on the chromium leachability of slags

As already mentioned, controlling the leachability of chromium represents an important task, however, the leachability of other elements such as vanadium is important too. Data from literature shows that vanadium cannot be bound in spinel type compounds, but it is possible to prevent it’s dissolution by adding CaO. The vanadium is bound in calcium silicates and their solubility decreases when other CaO compounds are present that dissolve easier. An exact metering is necessary in order to prevent the formation of free lime. Figure 9 displays the influence of the calcium concentration in the eluate on the leachability of vanadium.

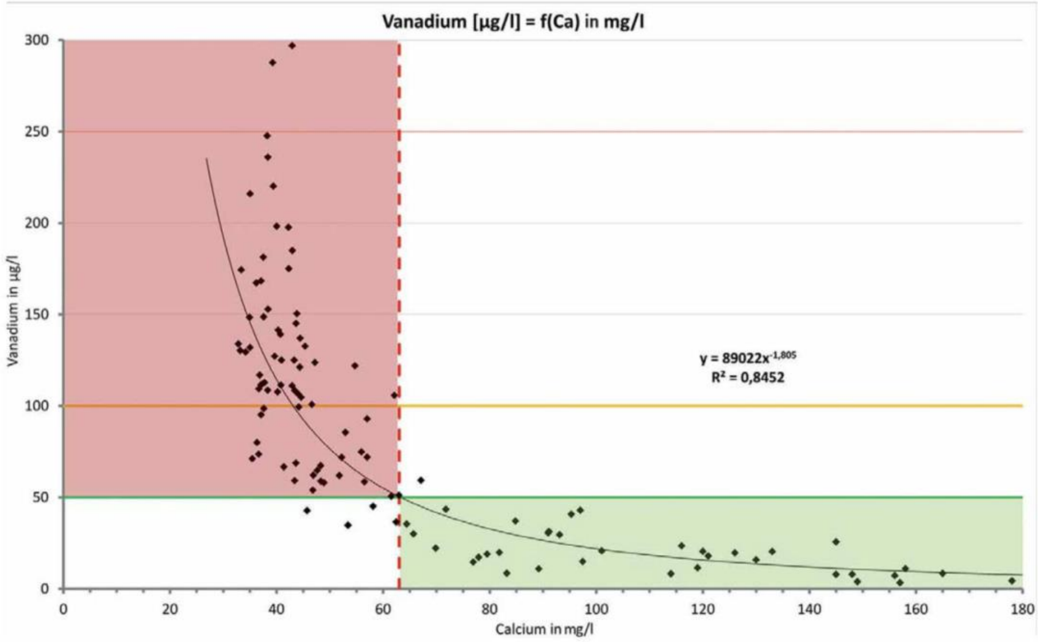

Figure 9: Leachability of vanadium depending on the calcium concentration in the eluate [9]

CONCLUSION

To summarize, two different routes for recovering valuable elements – mainly chromium - are present, the physical recovery and a pyro-metallurgical recovery process. However, the physical recovery process generates a fine grained slag and does not recovery the chromium oxide from the slag. This is why the resulting slag represents a hardly marketable product. On the other side the pyro-metallurgical reduction process requires considerations regarding the reducing agent, the process temperature and the usage of additives. Carbon represents a cheap reduction agent that shows promising results and is therefore favourable for an industrial scale treatment process. The temperature influences the thermodynamic equilibrium, the viscosity as well as the reaction kinetics. Generally, an increased temperature positively effects the reduction process, however, the processing costs also increase with an increasing temperature, which is why the temperature should be as low as possible and only as high as necessary. Additives also influence the reduction process. On the one side an increasing basicity increases the chromium oxide activity coefficients, but it also increases the liquidus temperature of typical high alloy EAF slags and may therefore lead to the formation of free lime. The addition of additives do not only influence the slags properties, but also influence its leachability. Depending on the concentration of heavy metal compounds the addition of Al_2O_3 or CaO may be mandatory. This overview shows that there are many parameters that must be considered in order to recovery valuable elements from the slag in order to generate two products, a ferroalloy and a marketable slag.

ACKNOWLEDGMENTS

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