Estimation of trace elements in unalloyed scrap

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Controlling the concentration of trace elements is crucial for the production of demanding steel grades like electrical or interstitial free steel. The charge mix of different scrap qualities and hot metal should minimize the risk of exceeding the limits of the trace elements chromium, nickel, molybdenum and copper. At the same time, it is crucial to optimize the choice of the input materials towards cost effectiveness.
Steel scrap can be highly inhomogeneous, which makes representative sampling extremely difficult. In addition to taking random samples at voestalpine Stahl GmbH in Linz a statistical approach to estimate the content of trace elements is utilized. Using hot metal-, steel- and slag-samples the concentration of the elements in scrap can be calculated. Assuming that these concentrations are distributed normal, the corresponding mean values and standard deviation can be estimated and is used in calculation models.
The outcome of this balance can be utilized for multiple purposes. Knowing the underlying distributions of the input materials makes it possible to determine a corresponding distribution of the raw steel. On a short term basis it is possible to detect unintentional mixing of alloyed and unalloyed scrap. Using this information, appropriate measures at the scrapyard can be taken. At the same time, the data over several years shows long term developments of certain scrap grades.

KEYWORDS: SCRAP – RECYCLING - TRACE ELEMENT – BOF – STATISTICAL MODELLING - PRODUCT QUALITY

INTRODUCTION: RECYCLING OF STEEL AND TRACE ELEMENTS

Steel is known for its ability to be multi-recyclable (1). Subsequently, from an environmental point of view, it is desirable to operate the LD-converter with high scrap rates. The voestalpine Stahl GmbH operates three LD-converters with a tapping weight of 175 t. During normal operation the amount of charged scrap ranges from between 20 to 30 % of the total metallic input.

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Fig. 1 – Steel's life cycle (1)

As illustrated in figure 1 scrap is "produced" during manufacturing (pre-consumer steel scrap) and the end of the product life (post-consumer steel scrap). Increased use of steel subsequently leads to an increased amount of available scrap. At the same time, many steel grades have high demands regarding the level of impurities, respectively narrow target windows for the concentration of alloying elements. These trace elements are not added deliberately to the steel and can have a negative effect on the material properties. Among the long list of possible trace elements those which cannot be removed using common steelmaking practice are especially important to control. The following table presents an overview of possible trace elements and its import sources (2).

Tab. 1 – Removability and source of trace elements (2)

element / input	W	Cu	Mo	Bi	Ni	Co	As	Sn	Sb	Cr	P	N	H	S	O	Pb	Zn	B	Nb	V	Ti	Si	Al	Ca
atmosphere												•	•		•									
stirring gas												•												
refractory													•		•							•		•
premelted heat	•		•		•		•			•						•					•			
ore							•		•						•									
scrap	•	•	•	•	•	•	•	•	•	•	•	•		•		•	•	•	•	•	•	•		
hot metal		•			(•)		•		•	•	•	•		•								•		
slag															•									•
additions											•		•	•	•							•		•
desoxidiser																							•	
alloying elements										•	•			•				•			•	•	•	
	non - removable						removable to a limited extent						easily removable											

Generally steelmaking offers two methods to extract elements which are dissolved in the melt. One pathway is through oxidizing reactions, which lead to a transfer of the element(s) into the slag phase. At steelmaking temperatures some elements can also be transferred into the gas phase and the vapor pressure of an element therefore plays a crucial role. The elements which cannot be removed are those which have a lower affinity towards oxygen compared to iron and those with low vapor pressures. Consequently to control the input of these elements is of great importance.

Table 1 also indicates that knowledge of the charge material is a key component towards control of steel quality, since the source of the majority of elements is the scrap. The selection of raw materials depends on a variety of factors, and often these additional criteria conflict with the desire to have a mix with low problematic trace elements. For instance:

◦ The metallic yield has been optimized along the entire production chain. This means that the amount of high quality pre-consumer scrap with known chemical analysis is lower nowadays.

◦ The input material should be as cost effective as possible. This means that the amount of low-quality post-consumer scrap is generally increasing.

◦ From an economic as well as environmental point of view the use of by-products such as slag or dust products (briquettes, granulate) is favorable. This leads to an increased input of trace elements.

◦ The demand for coated as well as high alloyed steels is high, which leads to an increased level of trace elements within the scrap. (3)

The following paper will present an approach to estimate the risk of excessive concentration of trace elements. Because of their high relevance in the steelmaking practice, the focus of this work will be on the elements Cr, Ni, Mo and Cu. Due to the highly inhomogeneous nature of scrap, sampling is difficult, time consuming and not representative. Therefor the mass flow and chemical analysis of all output- and input-streams at the LD-converter was observed.

SCRAP TYPES

In the present paper three different typs of scrap are analysed. The first scrap type is collected at different process steps within the production facility of voestalpine Stahl GmbH in Linz. The other two grades are aquired on the scrap market.

Tab. 2 – Analyzed scrap grades

scrap types			
type	origin	specification	type
1	internal	low alloy steel	pre-consumer
2	external	E6, E8	pre-consumer
3	external	E1	post-consumer

Different scrap qualities can be distinguished according to the european steel scrap spezification. Both E6 and E8 scrap are defined as thin new production steel scrap which is uncoated. According to the specification, the sum of the trace elements must be smaller than 0.3 [wt%]. In contrast to the quality E8, the quality E6 must be compressed into scrap packages in order to ease the charge of the scrap. E1 scrap is old used steel scrap with a thickness lower than 6mm. According to the specification, the copper content must be below 0.4 [wt%]. The upper bound for the sum of chromium, nickel and molybdenum is 0.3 [wt%]. (4)

MASS BALANCE

In order to calculate the concentrations of the elements Cr, Ni, Mo and Cu in alloyed scrap grades a mass balance was carried out. The input materials of the LD-process are hot metal, scrap, slag formers, cooling- and heating agents as well as oxygen. The output consists of a dust loaded off-gas, crude steel and slag. The composition of the different input– and output streams can be determined by the use of chemical analysis such as optical emission spectroscopy (OES) or X-Ray Fluorescence Spectroscopy (XRF). The frequency of the sample taking routine can differ significantly between the materials. Regarding the input materials the mass is measured by a crane scale or by the weighing system of the addition bins.

The determination of the quantities of the output streams is not that straightforward. The mass of the crude steel is weighted at the steel car after tapping. There has to be a correction in order to take the additions during tapping, slag carry-over and residual steel within the converter into account. For the mass balance of chromium, the amount of oxidized chromium must also be taken into account. Therefore knowledge of the slag mass is necessary. The mass of slag can be estimated by a CaO mass balance. For a more accurate estimation, knowledge of other oxides is taken into consideration as well. The exact procedures for the calculation of steel and slag masses are beyond the scope of this paper. Condensed information about the input and output streams is presented in table 2 and table 3.

Tab. 3 – input material

input			
material	quantity	composition	frequency
hot metal	weighted	OES	per heat
scarp	weighted	unknown	per heat
solid slag dust	weighted	XRF	per week
briquettes	weighted	XRF	per month

Tab. 4 – output material

output			
material	quantity	composition	frequency
dust	average values	XRF	per month
crude steel	weighted mass	OES	per heat
slag	balance	XRF	per heat

It can be deduced from the tables 2 and 3 that the quantities and compositions of all relevant material flows are known. The only exception is the composition of the scrap. Calculating a mass balance (difference between output and input) for all desired elements yields the desired composition.

(1)

$$x_{i_{SCRAP}} = \frac{m_{CS} \cdot x_{i_{CS}} + m_{SL} \cdot x_{i_{SL}} + m_D \cdot x_{i_D} - m_{HM} \cdot x_{i_{HM}} - m_{SCS} \cdot x_{i_{SCS}} - m_{DB} \cdot x_{i_{DB}}}{m_{SCRAP}}$$

xi	concentration of the element i		[wt%]
m	mass of the material flow		[kg]

CS	crude steel	HM	hot metal
SL	slag	SCS	solid converter slag
D	dust	DB	dust briquettes
		SCRAP	scrap

The mass balance [1] can be used for heats which consist only of hot metal and one type of scrap. Although scrap types of lower quality are only used to a limited extend and are often not charged alone, this method is still beneficial in order to gain knowledge about these types. An example of a scrap type which is only used to a limited extent is type 3, while the type 1 and type 2 scraps are used in larger quantities.

Mixture of scrap types

For the case described above the concentration x_{iSCRAP} consists of different scrap types. Some scrap types are taken as input parameters for a mixed mass balance. These are types where a significant amount of heats are produced, which have this scrap type as sole solid metal input. Assuming we have a scrap mixture which consists exclusively of scraps which we can use as input and only one unknown scrap type the result of [1] can be used as input for a mixed mass balance. The equation [2] shows the approach for calculating the concentration of less frequently used scrap qualities.

(2)

$$x_{i_{type\ a}} = \frac{x_{i_{scrap}} \cdot m_{SCRAP} - \sum_{j=1}^{n} x_{i_{type\ j}}\, m_{i_{type\ j}}}{m_{i_{type\ a}}}$$

The mass respectively concentration of these less used scrap qualities are denoted by $m_{itype\ a}$ and $x_{itype\ a}$.The most important parameter in equation [2] which is required is the concentration of every element i within the scrap type j. For this calculation the result of the last heat where exclusively type j scrap was used is taken. Using equations [1] and [2] the concentrations for a significant number of heats can be calculated. These results are then taken as inputs for a statistical analysis of the underlying elemental distributions within the various scrap types.

STATISTICAL APPROACH

Smooth kernel distribution

Having calculated the content of numerous scrap charges the question arises whether it is possible to calculate the underlying probability density function. A method to get such a function is the use of kernel density estimation (KDE), which is a well described non-parametric approach (5). This means that no prior knowledge of the underlying distribution is necessary. The idea is to create a function which itself is a mixture of continuous distributions. We consider the independent samples X1, …, Xn and calculate the density function by using equation [3].

(3)

$$\hat{p}_n(x) = \frac{1}{n\,h} \sum_{i=1}^{n} K\left(\frac{x - x_i}{h}\right)$$

The amount of smoothing is controlled by the smoothing bandwith h>0. K is a probability density function called kernel. One of the most common functions used as K is the so called Gaussian kernel.

(4)

$$K(u) = \frac{1}{\sqrt{2\pi}} e^{-\frac{u^2}{2}} \text{ where } u \in \mathbb{R}$$

In contrast to selecting various kernel functions, which only has a marginal influence on the outcome in most cases, the value of the bandwidth h has to be chosen carefully (5). Fig. 2 illustrates the influence of different factors on the resulting KDE for the approximation of a discrete distribution.

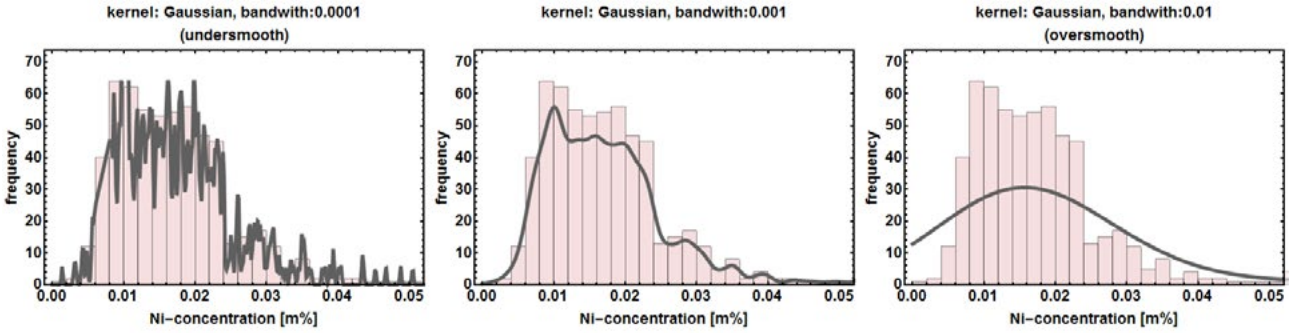

Fig. 2 – Influence of the bandwidth on the KDE

Methods to determine to smoothing factor automatically do exist. To determine the distributions which are used in the present paper, this factor was chosen manually in order to guarantee a consistent result.

Normal distribution

The kernel densities are mixtures of probability densities and therefor are probability densities themselves.

Nevertheless for some application it is beneficial to approximate the KDE with a single normal distribution. This makes it easier to illustrate the outcome of the calculations and at the same time the results can readily be implemented in existing models. To approximate the underlying distribution there are quite a few possibilities. Two approaches have been tested. In order to obtain the first fit (fit 1) the minimization problem [5] was solved.

(5)

$$\sum_{i=0}^{10^3}\left(KDE\left(i \cdot \frac{upperLimit}{10^3}\right) - f\left(i \cdot \frac{upperLimit}{10^3}\right)\right)^2 dx \rightarrow Min. \text{ where } f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

The second approach is to find the best fit for the cumulative distribution (fit 2), which is described using equation [6].

(6)

$$\sum_{i=0}^{10^3}\left(\int_{-\infty}^{i \cdot \frac{upperLimit}{10^3}} KDE(x)\, dx - \int_{-\infty}^{i \cdot \frac{upperLimit}{10^3}} f(x)\, dx\right)^2 \rightarrow Min. \text{ where } f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

For both minimization problems the Nelder Mead global optimization algorithm (6) was used to determine μ respectively σ. The increment for the discretization was chosen as $upper/Limit/10^3$, which is a compromise between accuracy and computation speed. The $upperLimit$ is the highest observed concentration. Fig. 3 shows a comparison of the two methods for one of the distributions.

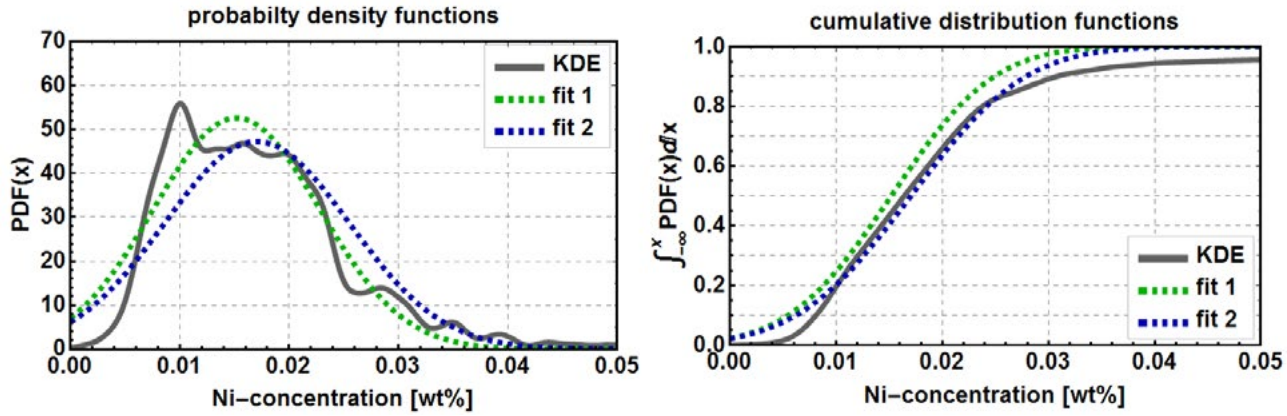

Fig. 3 –Approximation of a KDE

Visual inspection of several approximations showed that generally fit 2 maps the underlying distribution better. The tail on the right side of the distribution originates from rather high concentrations. These values can be a consequence of contamination of the scrap (e.g. plated steel sheets) or are consequences of a false classification. These events can't be mapped by a normal distribution since the probability density function is strictly monotonous.

RESULTS

The presented logic was used to calculate the mean value and standard deviation for three scrap types as well as for the hot metal. In the case of the hot metal the concentrations for every heat are measured. The distributions were calculated using the methods presented in the paragraphs above.

Tab. 5 – Mean and standard deviation per input material

scrap composition								
	type 1		type 2		type 3		hot metal	
element	μ [wt%]	σ [wt%]	μ [wt%]	σ [wt%]	μ [wt%]	σ [wt%]	μ [wt%]	σ [wt%]
Cr	0.0668	0.0328	0.0605	0.0242	0.1739	0.1522	0.0275	0.0054
Ni	0.0177	0.0091	0.0192	0.0081	0.0884	0.0423	0.0053	0.0017
Mo	0.0048	0.0040	0.0044	0.0033	0.0150	0.0121	0.0017	0.0015
Cu	0.0195	0.0047	0.0177	0.0052	0.2170	0.1025	0.0044	0.0015

Type 1 und type 2 can be considered as high quality scrap which show relatively low concentrations of trace elements. The concentrations of these two scrap grades are relatively similar. Compared to hot metal, the concentrations are between 2.4 (chromium) and 4.4 (copper) times higher than those of the hot metal. Type 3 is a post-consumer scrap and therefor the load of trace elements is significantly higher. Especially significant, is the difference regarding the copper concentration which is 12 times higher in type 3 compared to type 1 and type 2 scrap. Despite these higher trace element values, the use of type 3 scrap can provide an economic advantage since its price is comparably low.

Besides being a useful method to estimate the input of trace elements for both individual scraps and mixture of scraps, it is also helpful in tracking long term trends regarding the composition of different scrap types. It can be seen that generally the amount of copper in unalloyed steel scrap decreased over the past years. The reason might be increased efforts of scrap recycling companies to minimize to contamination with high copper materials like wires or parts of electric engines. At the same time it can be observed that the molybdenum concentration is increasing. In the case of the voestalpine Stahl GmbH the most important source of pre-consumer scrap is the automotive industry. While molybdenum is usually not used as an alloying element for steel-qualities which are used for the outer skin of a vehicle, it is added to high strength steels which are used for structural parts. An example is dual-phase steels where molybdenum delays the formation of ferrite and pearlite, which has an positive effect on the hardenability (7) .

The following paragraph shows a method to calculate the estimated distribution for arbitrary input material mixes. The method is especially useful in quantifying the risk of an excessive trace element concentration.

ESTIMATION OF RISK

The advantage of obtaining normal distributions, as presented in the preceding paragraphs, is that they can be readily used for further calculations. For example, it is possible to calculate the probability that the concentration of a specific element will be exceeded for a specified raw material mix. Since the distributions of all input materials are known, the distribution of the crude steel can be estimated. It is a well-known fact from statistics that the linear combination of normal distributions is again a normal distribution. This holds also if we add weights to the normal distributions. So we would like to calculate $S = \sum_{i=1}^{n} p_i \cdot c_i = 1$ where $C_i \sim N(\mu_i, \sigma_i^2)$ and $S \sim N(\mu_S, \sigma_S^2)$ are normal distributions where μ is the mean and σ the standard deviation. The parameters μS and σS can be calculated using the following formulae:

(7)

$$\mu_S = \sum_{i=1}^{n} p_i \mu_i \text{ and } \sigma_S^2 = \sum_{i=1}^{n} p_i^2 \sigma_i^2$$

Using the information from table 5 the distribution of an arbitrary charge-mix can be calculated. The following figure illustrates the probability of exceeding the limits for nickel which are 0.02 respectively 0.03 [wt%]. While 70 % of the input is hot metal for the remaining 30 % the amount of type 3 scrap varies between 5 and 20 %. The rest consists of type 1 scrap. Making use of the cumulative distribution function a quick picture of the situation is possible.

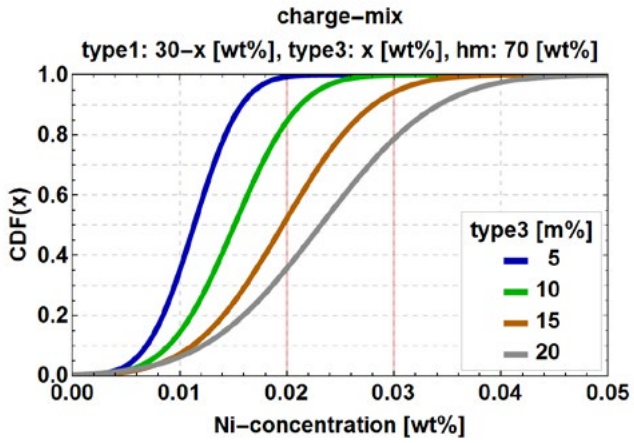

Fig. 4 – Cumulative Distribution of the Ni-content

It can be seen that a concentration below 0.02 [wt%] is quite unlikely (below 50 % probability) if the amount of type 3 scrap exceeds 15 %, while adding 5 % of type 3 scrap should be acceptable. If higher limits are tolerable the amount of type 3 scrap can be increased. Fig 4 is also an example of a possible scenario, taking the limit of a certain element as input it would be a straightforward calculation to determine the maximum amount of a certain scrap type in order to keep to risk of exceeding this limit below a certain threshold.

CONCLUSIONS

The paper presents an approach for the estimation of trace elements in scrap which can be used in LD- or EAF-steelmaking. The presented approach is statistical in nature, and although singular events like the mix-up of different scrap grades cannot be predicted, this method provides a reliable routine of characterizing scarp mixes and overcomes many of the issues associated with scrap characterization by manual sampling alone. It is also obvious that in order to ensure a cost effective input mix, scraps of varying quality should be selected, however this often increases the risk of exceeding specified upper bounds for various trace elements, particularly for certain steel grades. The advantage of the presented method is that this risk can be quantified. Another area of application is the analysis of long term trends regarding the composition of certain scrap grades.

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