

## **POSSIBLE ALTERNATIVE SECONDARY RESOURCES FOR THE PRODUCTION OF FERROALLOYS**

**\*Gernot Rösler<sup>1</sup>, Manuel Leuchtenmüller<sup>2</sup>, Jürgen Antrekowitsch<sup>3</sup>**

<sup>1</sup>Dr., <sup>2</sup>Dipl.-Ing., <sup>3</sup>Priv.-Doz.

*Christian Doppler Laboratory for Optimization and Biomass Utilization in Heavy  
Metal Recycling, Chair of Nonferrous Metallurgy, Montanuniversitaet Leoben,  
Franz-Josef-Str. 18, 8700 Leoben, Austria*

(\*corresponding author: gernot.roesler@unileoben.ac.at)

### **ABSTRACT**

Elements such as Cr, Mn, Ni are commercially used as alloying elements in the (special) steel industry, in order to increase the performance of the finished steel product. Since alloying a liquid iron bath in a steel mill using pure metals (Cr, Mn, Ni) is far too expensive, so-called ferroalloys are available which are much cheaper and easier to produce. These alloys are typically standardized and traded at the London Metal Exchange, similar to pure metals. Usually, primary resources (ores) are used to produce ferroalloys, however, due to shortages at the raw material supply, environmental issues, etc. secondary resources should be focused in detail to serve as possible raw material for the production of ferroalloys. This paper will deal with possible complex residues which may be used for this purpose.

### **INTRODUCTION**

The Chair of Nonferrous Metallurgy at the Montanuniversitaet Leoben/Austria has a long year experience in the recycling of “standard” steel EAF dust as well as further complex residues such as dust from the foundry and copper industry. The logic consequence is to focus also on dust from special steel plants in a subsequent step. The big difference of this type of dust is the quite high amount of alloying elements, since they are mostly charged (as ferroalloy) during smelting in the EAF. In contrast to ordinary EAF dust, zinc is relatively low and therefore not always interesting for Waelz kiln operators. The challenge at recycling special steel EAF dust is, that each EAF batch might be different, because the produced lot sizes of one steel quality are relatively low.

Furthermore, when thinking about this type of residue respectively its chemical composition, several other potential resources with elements like Cr, Ni and Mn came up such as dust, slags and scales from the ferroalloy industry or also very untypical ones, like tailings. In doing so, a completely new research area can be explored in the future: the characterization and process development of Cr, Ni and Mn containing residues with subsequent simultaneous recovery to produce a ferroalloy.

Of course, much more elements are available which serve as main element in a ferroalloy. Therefore, this publication will focus on the major alloying metals – Cr, Ni and Mn which keeps the available secondary resources in a manageable size.

Beside already applied techniques, such as recycling of industrial or automotive catalysts to recover Ni and V, further materials with higher complexity are available

in order to recycle alloying elements such as Cr, Ni and Mn. Therefore, new or adapted processes have to be found to recycle these potential secondary resources.

In the following, the results of a literature survey carried out recently should point out possible resources as well as already existing / proposed recycling methods available.

## POSSIBLE SECONDARY RESOURCES

In general, the mentioned literature survey resulted in the division of the occurring residues in four categories:

- dust and sludge (fine particles, often only available as sludge due to off-gas treatment)
- slags (liquid, which makes a treatment on-site just after tapping possible)
- scales (solid, high purity) and
- miscellaneous resources

The following chart in Fig. 1 gives a rough overview of the typical residues which could arise during a metallurgical process. There may be more residues available that are not listed below, however, many metallurgical companies do not publish any data regarding their residues. The following subchapters will describe the following figure in more detail.

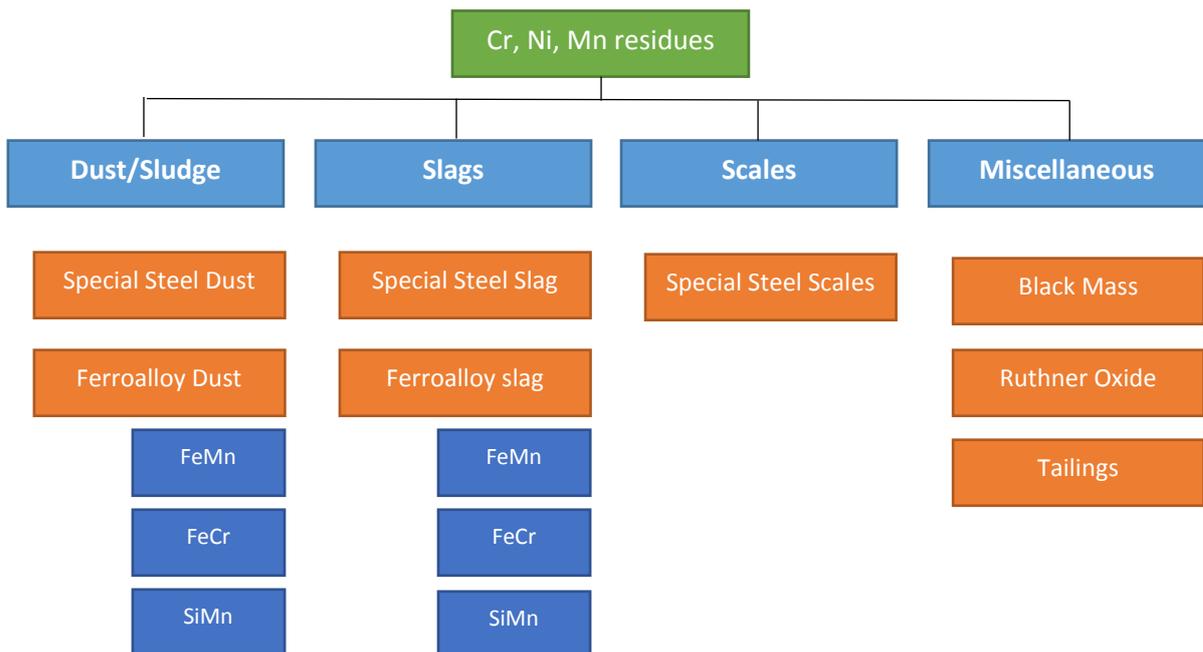


Fig. 1

Overview of possible secondary resources for the production of ferroalloys

### *Dust/Sludge*

Within this paragraph, an overview of the selected possible secondary resources based on figure 1 is represented. Here, two major types of dust could be identified – special steel dust and dust/sludge from the ferroalloy industry. The following table 1 gives an overview on typical chemical analysis that are produced within this industry.

Tab. 1: Overview on selected types of dust and their average composition (own research and [1–5])

	Cr <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
FeMn dust	<0.06	0.45-2.70	1-5	2-4	4-40	1-4	-
FeCr dust	4.65-20.40	3.00-17.63	8.93-28.49	0.66-25.60	10.60-47.90	1.20-11.52	0.12-0.44
SiMn dust	0.03	1.32	12.15	3.11	31.70	3.37	-
Stainl.steel dust	14.50-16.37	35.64-46.44	-	-	-	-	-
	MnO	NiO	ZnO	PbO	Cu	Na	K
FeMn dust	20-70	-	0.62-7.47	<0.6	~0.05	0.37-1.89	2.49-9.13
FeCr dust	0.23-0.48	0.09-0.17	1.87-9.40	0.02-0.13	~0.03	<5.94	<3.06
SiMn dust	26.64	-	1.94	0.15	~0.02	1.94	8.94
Stainl.steel dust	-	2.80-6.75	0.50-6.47	-	-	-	-

### Slags

Similar, the following table 2 represents available quantities of elements at different slags occurring in the metallurgical industry, according to figure 1.

Tab. 2: Overview on selected types of slag and an average composition [6–10]

	Cr <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
FeMn slag	-	12.97	0.56	8.21	13.84	5.35	0.27
FeCr slag	0.01-13.50	1.80-3.98	10.3-33.23	0.5-5.86	28.89-42.1	0.95-29.64	0.14-0.33
SiMn slag	-	0.4-0.8	4.2-5.5	13.5-17.0	18.1-49.2	7.2-8.1	-
Stainl.steel slag		35.64-46.44	-	-	-	-	-
	MnO	NiO	ZnO	PbO	Cu	Na	K
FeMn slag	31.82	0.01	0.05	0.05	0.01	-	-
FeCr slag	0.17-0.42	-	-	-	-	<0.29	<0.19
SiMn slag	13.6-16.1	-	-	-	-	-	-
Stainl.steel slag	-	2.80-6.75	0.50-6.47	-	-	-	-

### Scales

Scales are “produced” during the solidification and heat treatment of metals due to the application of natural gas / (oxygen-enriched) air burners previously to a rolling mill. The chemical composition equals usually more-or-less the steel composition as it can be seen in table 3.

Tab. 3: Overview on a typical chemical composition of scales

	Cr <sub>2</sub> O <sub>3</sub>	FeO	NiO
Stain.steel scales	12.57	73.03	3.69

### Miscellaneous

The following list of “miscellaneous” material is an enumeration of possible resources for the production of ferroalloys, however, making no claim to be exhaustive.

Tab. 4: Overview the elemental distribution of miscellaneous available material ([11–13] and own research results)

	Cr <sub>2</sub> O <sub>3</sub>	FeO	MgO	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	S
Black Mass	-	0.09-0.64	-	-	-	-	-
Ruthner oxide	12.86	66.26	-	-	-	-	-
Tailings	0.29	42.97	-	0.14	5.84	3.40	10.00
	MnO	NiO	ZnO	PbO	Cu	Na	K
Black Mass	33.57-58.12		14.94-35.23	<0.03	-	-	-
Ruthner oxide		5.60	-	<0.11	-	<0.29	<0.19
Tailings	-	4.71	-	-	0.38	0.4	0.6

## POSSIBLE PRETREATMENT OF AVAILABLE SECONDARY RESOURCES

One challenge will be the utilization of the aforementioned material into a metallurgical process respectively a furnace. To decrease a carry over at pyrometallurgical processes, agglomeration concepts have to be developed or adapted. Beside thermal agglomeration (sintering) growth and pressure agglomeration can be applied. The first mentioned method, however, is used very rarely due to the complex composition of the secondary raw material. Due to varying softening/melting/vaporization temperatures of each species present in the material, a unique sintering process is hard to realize. In the following, the two other possible methods are described, since these ones are more likely.

### *Pelletizing*

This method belongs to the growth agglomeration. Very often, simply water is applied as binder, other possibilities may be exemplarily bentonite or clay. The secondary raw material is mixed with the mentioned additives and rolled in a pelletizer disk. The so produced green pellets have to be dried in order to increase the resistance against compression [14].

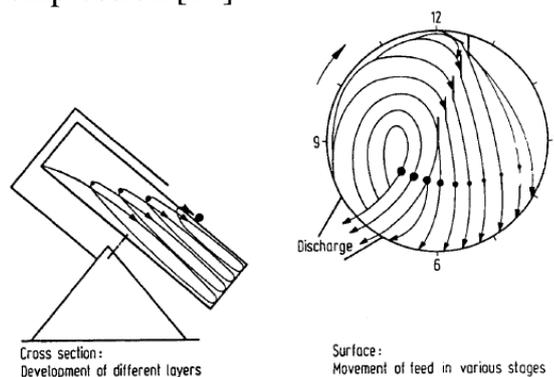


Fig. 2

Schematic drawing of the pelletizing process. The arrows show the movement of the agglomerated residue in dependence of its size until it is discharged [14]

### *Briquetting*

In contrary to the previous mentioned method, briquetting is a pressure agglomeration. Here, the fine powdered material is mixed with binders similar to the pelletizing as well, but in a higher quantity which results in a more plastic

behaviour. Afterwards, the agglomeration is performed with a ram or a briquetting press. The received agglomerate is dried at ambient temperature for some days and then ready to be fed into the recycling furnace [14].

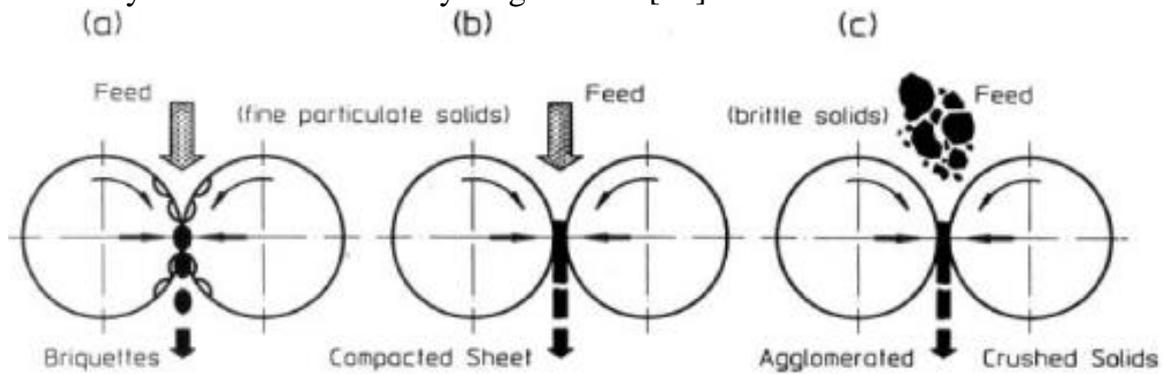


Fig. 3

Overview of different briquetting methods: a) egg-shaped briquettes b) sheet briquetting c) crushing/pressure agglomeration [14]

### Optimization

Further advantages beside the improvements of a better chargeability can be found when mixing the residues with slag forming additives or even carbon carrier for reduction purposes in advance. Due to a very homogeneous distribution of residue, slag additive and carbonaceous material, better reduction rates and lower burn off rates can be achieved. Figure 3 shows a SEM picture of a briquette enriched with carbon short after briquetting and after 1000 °C in a neutral (nitrogen) atmosphere. It can be clearly seen that a pre-reduction is achievable by this improvements.

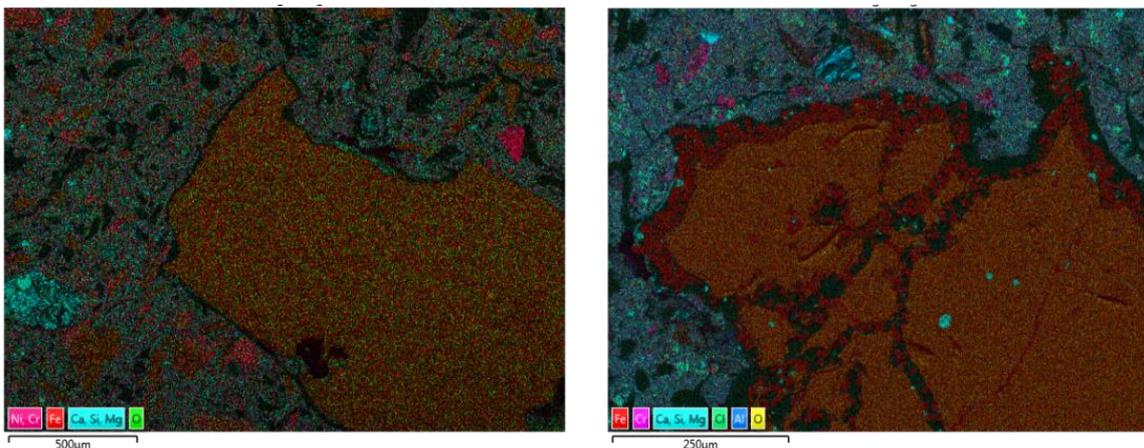


Fig. 4

Scanning electron picture of a intersectional view of a self-reducing briquette short after briquetting (left) and after heat treatment at 1000 °C (right)

## POSSIBLE FURNACE TECHNOLOGIES

This chapter will focus on smelting/reduction technologies; however, possible pre-treatments such as clinkering or roasting are not mentioned. In principal, a literature review shows two available methods for processing the aforementioned

types of residues. Due to the high melting range of the metals associated to these wastes, two high power consuming types of furnace can be mentioned:

- Submerged Arc Furnace (figure 5)
- Plasma based furnace (figure 6)

Both types of furnaces are able to generate high temperatures which makes it possible to melt down and reduce the valuable metals, respectively. The big difference between these furnaces is the way of charging material into the furnaces. The submerged arc furnace needs bigger particle sizes which makes an agglomeration mandatory due to a necessary gas permeability. This would lead to an obligatory pelletizing or briquetting process for using this material in this furnace type. In contrary, bigger feed material like slag can be forwarded to the furnace without any pre-treatment.

However, the feed material of the plasma arc furnace are small particles which is perfect for utilizing dust or scale. In this case, bigger particles have to be crashed in advance to be suitable for this furnace type.

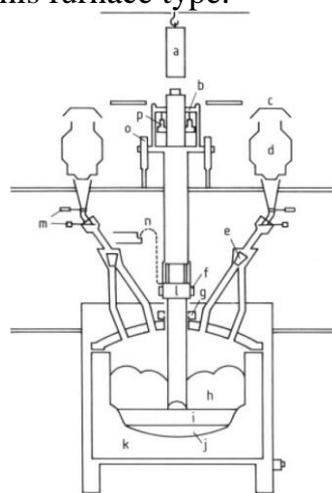


Fig.5

Drawing of a FeNi DC submerged arc furnace

- a) Electrode addition; b) Holding ring; c) Ventilation hood; d) Calcine car;  
 e) Charge diverter bucket; f) Pressure ring; g) Ventilation ring; h) Calcine; i) Slag; j)  
 Metal; k) Refractory; l) Contact clamp; m) Change valves; n) Bus; o) Electrode hoist; p)  
 Slipping ring [15]

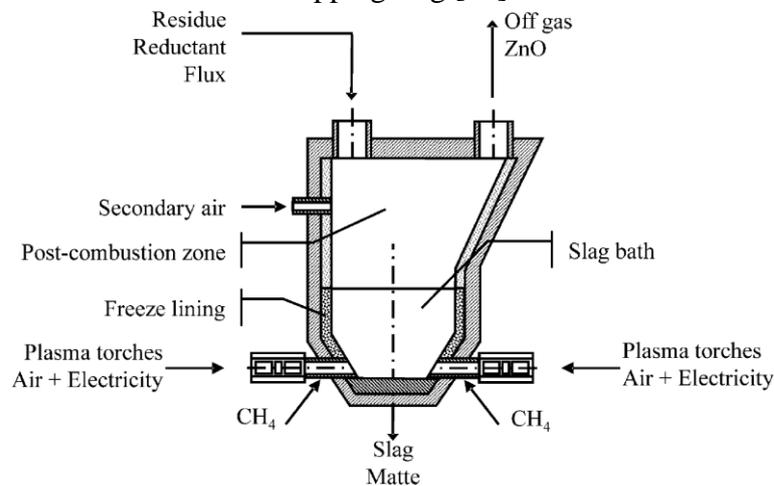


Fig. 6

Set-up of a plasma operated shaft furnace for the production of ferroalloys from stainless steel residues [16]

Both types of furnaces have a relatively high power consumption, leading to the conclusion that a highly efficient process has to be performed in order to recover the mentioned elements in an economic way.

## CONCLUSION

This paper reviews possible secondary resources for the production of ferroalloys. At the moment it is very difficult to get any representative quantity of residues available, estimations concerning resources can be made for slag and dust from the ferroalloys industry. Here 28.7-51.7 Mt can be assumed based on the fact that the slag/metal ration at SAF operations can be set to 1-1.8 for the annual world production of FeCr, FeMn and SiMn in 2013. Moreover, 0.4-0.6 Mt of dust is generated at the same year (15-25kg/t) [17].

For the stainless steel industry, similar approaches can be made. 2014, 41.7 Mt of stainless steel was produced. This leads to the fact that in between 0.63-0.83 Mt of dust are generated, which are partially treated by the Waelz process to recover mainly zinc. Beside, 5.8 Mt of stainless steel slag was produced 2014 when expecting ~140 kg/t steel. Not included in this assumption are other slag types produced at stainless steel operations such as AOD slag [18].

However, high quantities of material would be available for the proposed recycling process. In advance of the metal recovery, additional beneficiation routes have to be applied to increase the value of the material fed into the furnace. This would lead to a much more efficient and economic process, leading to a sustainable procedure for residues from the ferroalloy and stainless steel industry.

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