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SWEREA MEFOS PERSPECTIVE ON METAL RECOVERY FROM SLAGS

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Abstract

Every year the metallurgical industry generates huge amounts of slag. The annual amount of generated steelmaking slags alone is more than 150 million tonnes and contains more than 20 million tonnes of iron, 6 million tonnes of manganese and 1 million tonnes of phosphorus. Full utilisation of this huge amount of a by-product is limited by its leaching properties and volume stability and the existence slag utilisation markets. Swerea MEFOS has in the past 20 years developed a large number of recycling processes based on large scale tests using the various pilot reactors available at the institute. The waste materials treated include almost all wastes generated within the steel productions and also a large number of residues including hazardous liquid waste from other metal industries and sectors. Some of these processes will be highlighted in this paper with a special focus on metal recovery from slags.

Introduction

Slag is a by-product generated during metal production. A huge amount of various slags is produced all over the world. The annual amount of generated steelmaking slags alone is more than 150 million tonnes. Based on this and on an average analysis of steel slag, globally the steel slag alone should contain more than 20 million tonnes of iron, 6 million tonnes of manganese and 1 million tonnes of phosphorus. Full utilisation of this huge amount of by-product is limited by its leaching and volume stability properties and the market situations. In addition to these metals, the yearly disposed Swedish BOF-slag alone contains about 5000 tonnes of vanadium, which with a vanadium price of about 30 US$/kg V corresponds to a market value of 150 million US$. Since the mid 1990s Swerea MEFOS has been involved in many projects aiming for efficient metal recovery and increased slag utilisation. These projects included slag stabilisation to improve the physical and leaching properties, slag reduction for metal recovery, dry slag granulation for heat recovery and for reduced leaching of heavy metals, water granulation for production of raw materials for cement industry and transforming of hazardous wastes into useful slag formers products. Some of these projects will be highlighted in this overview.

Recovery of Vanadium from Swedish and Finnish BOF-slag

Due to the use of LKAB pellets, which contains about 0.1% V, the Swedish and Finnish BOF-slag has a vanadium content of 2-3%. During the last 40 years there have been many R&D activities on vanadium recovery from the Swedish BOF-slag. This activity was further intensified in the end of 1990s when Swerea MEFOS initiated the well-known IPBM-project[1] followed by the 8 years VILD-project[2] (2004-2012). The IPBM (**I**n-**P**lant **B**y-product **M**elting process) project was financed by ECSC (today RFCS). The VILD (**V**anadium **I**n **LD**-Slag) project was financed by MISTRA (Swedish Foundation for Strategic Environmental Research) and the steel and mining industry in Sweden and Finland. The methods developed and some test results from these two projects will be described in the following paragraphs.

The IPBM is a standalone process aiming for processing of all in-plant by-products including steel slag. The idea is to recover metals from the slag and modify the slag to a valuable product. As all the other fine grained residues generated in the steel plants together represents about 20-25% of the slag amount, it is also the intention of the IPBM-process to include treatment of these residues, see Figure 1.

The furnace applied is a DC-furnace with hollow electrode. Wastes or by-products from the iron- and steelmaking process are fed through the hollow electrode, passing through the hot DC-arcs, and are melted and reacted immediately. The valuable elements are concentrated in the metal phase and the rest of the reduced slag is modified according to the targeted composition. The more volatile elements, like zinc, lead, cadmium, alkalis and halogens in the dust, will be evaporated and are collected in the filter system.

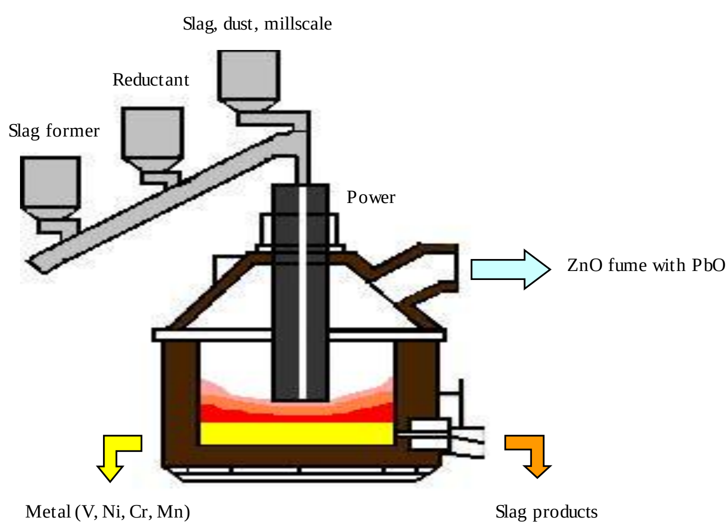


Figure 1: The IPBM-process using a DC-furnace with hollow electrode

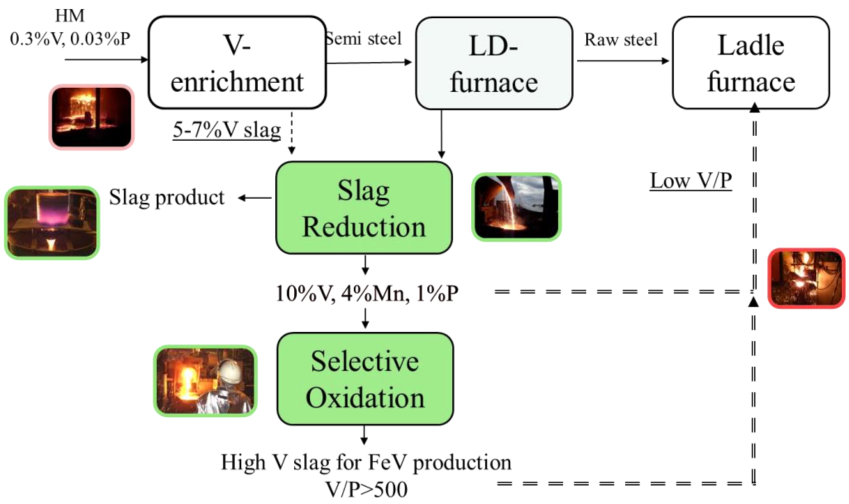


Figure 2: The research activities of the VILD-project

The activities in the VILD-project are described in Figure 2. As shown it contains following activities:

- Further development of the cold slag reduction process including the DC-furnace technology
- Direct hot slag reduction with and without electric furnace
- P and V-separation
- V-enrichment
- Direct use of FeV with an increased P-content

Processing of cold slag using a DC-furnace

Recovery of vanadium from Swedish BOF-slag has been developed in the IPBM-project. The experimental set-up of the 3 MW DC arc furnace at Swerea MEFOS is shown in Figure 3. This concept was further tested and verified in a recently performed pilot campaign for co-treatment of BOF-slags and BF-sludge within the VILD-project. The reductants being tested included anthracite and silicon carbide (SiC). Small amounts of ferrosilicon and aluminium were also added in the final stage in some of the trials. The purpose was to investigate the lowest possible residual V-content in the slag that could be achieved. Slag formers used for the slag modification were silica sand and bauxite.

Over the years, a large amount of BOF-slag has been treated in several test campaigns. In the VILD-project, about 15 tonnes of a V-enriched slag, called LUVA-slag, was also successfully pilot tested. These pilot tests have confirmed that the DC-furnace is a powerful reduction tool for the recovery of vanadium from steel slags.

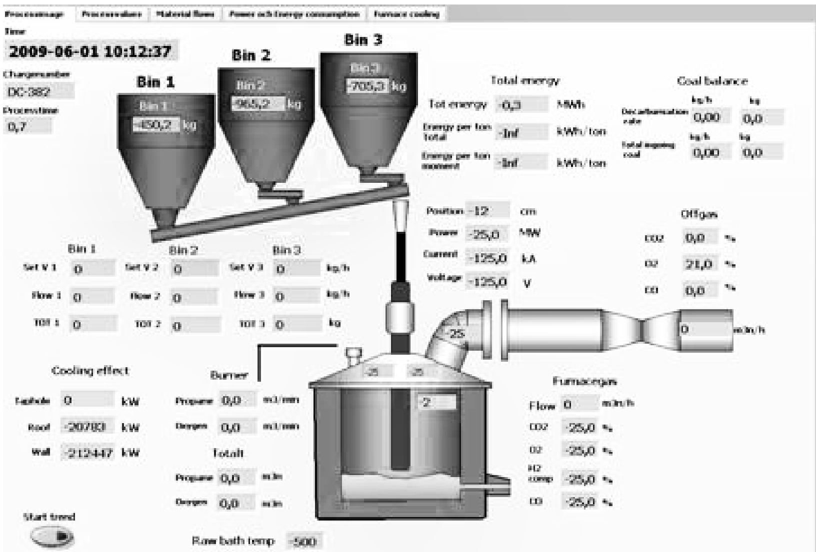


Figure 3: Experimental set-up of the DC-furnace for slag reduction

The reduction degree and slag composition were easily controlled by the reductant/slag ratio and the addition of slag formers. Blast furnace sludge (BF-sludge) was also treated in some of the trials for metal recovery and as additional carbon source. Some of the test results obtained from the DC-furnace tests are summarised in Table 1.

The anthracite/slag rate was about 130 kg/tonne slag and the energy consumption at a feeding rate of 1 tonne cold BOF-slag per hour was about 1.6 MWh/tonne. The heat losses through the furnace wall, tap-hole and roof were about 400 kWh. Less slag additives and subsequently less energy was needed for treating the LUVA-slag due to lower basicity (~1.6) compared to the BOF-slag (~4). The SiC/slag rate was about 110 kg per tonne of slag and the energy consumption at a feeding rate of 1 tonne BOF-slag/h was about 1.2 MWh/tonne. The heat losses were 370 kWh.

Table 1: Summary of the major test results

	V-recovery %	Energy cons. MWh/tonne slag	Flexibility	Reductants
LD-slag	>90%	1.3	Excellent	C, C+FeSi, C+Al, C+SiC
	>90%	0.9	Excellent	SiC
LUVA-slag	>90%	1.2	Excellent	C, C+FeSi, C+Al
	>90%	0.9	Excellent	SiC

For each tonne BOF-slag processed, about 220 kg of metal with up to 10% vanadium will be obtained and about 800-1000 kg of slag product is formed, depending on the target slag composition. If LUVA-slag is treated, a metal with up to 15% vanadium will be obtained. To ensure the targeted low V-content in the slag (<0.1%), a small

amount of FeSi or Al can be added in the end of the process, which has been also successfully tested.

Direct hot slag reduction

The hot slag reduction aims at efficient use of the sensible energy in the molten slag which has a heat value of about 600 kWh/tonne slag. The hot slag reduction has been initially tested in a 2 tonne slag scale in 1999 using a very simple set-up at Swerea MEFOS. The obtained results was quite encouraging, with a vanadium recovery of 60-80% and over 90% of iron. A metal with about 5-6% V was obtained.

In the current VILD-project, a large number of hot slag reduction tests have been performed at Swerea MEFOS and at SSAB EMEA in Luleå. The various test set-ups for the hot slag reduction trials are shown in Figure 4.

Figure 5 shows the produced metal and slag from one of the plant trials performed at the SSAB EMEA works in Luleå. The main observation from the trials is that the ignition of the reaction between the added FeSi and the hot BOF-slag is extremely important for the success of the process.

Plant trials - tapping

Plant trials - injection

Pilot trials - Kaldo

Pilot trials - injection

Figure 4: Different experimental set-ups for the direct hot slag reduction test campaigns[3]

Figure 5: Produced metal and slag from one of the industrial trials using FeSi75

The best results were obtained in the test where aluminium was added during tapping. Vanadium in the slag could be reduced to about 0.1% but also a significant reduction of SiO_2 occurred. The metal product also had a high content of aluminium and vanadium, about 8.5%, phosphorus 1% and manganese 6.5%. These figures indicate that excellent reduction results were feasible. The reaction was, however, quite violent and a large amount of heat was generated. It was hard to control the reduction degree and the process temperature.

In order to have a better temperature control, injection of FeSi powder into hot molten BOF-slag has also been performed, both in pilot scale (2 tonnes of slag at Swerea MEFOS), and in full scale (10 tonne of BOF-slag at SSAB EMEA in Luleå).

The reason for the use of a Kaldo furnace to treat hot slag is that the furnace is relatively simple and it is possible to control the retention time. It was, however, shown that the retention time did not improve so much the recovery degree of vanadium. The main reason is probably due to the high slag volume in relation to the metal volume in the bottom of the reactor. In general, the slag/metal weight ratio is about 4 to 1, which corresponds to a slag/metal volume ratio of about 12 to 1. This means that the reaction interface of slag and metal is too small to get an efficient reaction.

The experiences from the direct hot slag reduction trials are summarised in Table 2. Generally speaking, it could be concluded that it is possible to obtain good reduction results but it is not easy to control the process as you only have one single chance to ensure success of the trials. Everything has to be correct to get the perfect reduction conditions. Another possible reactor for this will be the so called zig-zag furnace system, which consists of two ladles, reladling to each other, to and fro until the reaction is completed. This has been used for production for LCFeCr. However, this is quite complicated.

Table 2: Main observations from the direct hot slag reduction trials

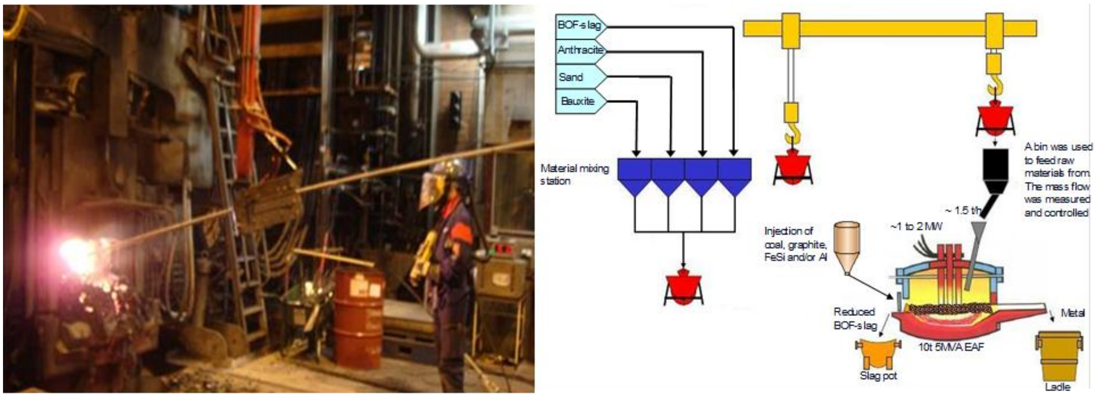
	Fe- and P-recovery	V-recovery	Temperature control	Comment
Tapping - FeSi	Excellent	Poor	Poor	Ignition important
Tapping - Al	Excellent	Excellent	Poor	Violent reactions
Injection – pilot	Excellent	Moderate	Excellent	Need better V-recovery
Injection – SSAB	Excellent	Moderate	Excellent	Need better V-recovery
Kaldo - pilot	Excellent	Poor	Excellent	Poor slag/metal mixing

Cold and hot slag processing using an AC arc furnace

In order to further improve the controllability of the reduction degree and the process temperature, the hot slag reduction was also simulated in an electric arc furnace. About 24 tonnes of BOF-slag with high V-content was treated in 21 trials in two test campaigns using the 5 MVA AC arc furnace at Swerea MEFOS. The experimental set-up is shown in Figure 6. The advantages of using an AC- or a DC-furnace instead of the direct treatment methods during tapping or by injection is the possibility to treat both cold and hot BOF-slag, use of carbon based and cheaper reducing agents, improved process control and higher degree of flexibility to compose different slag products. Various process parameters, such as reducing agents and slag basicity, have been investigated.

The BOF-slag, slag additives (silica sand or bauxite) and in some cases anthracite (treatment of cold BOF-slag) were fed on a 5 tonnes steel bath with low carbon content via a chute positioned in the middle of the three electrodes. Slag additives were chosen, aiming for a liquid slag at a process temperature of 1650°C and for the desired slag properties. Final reduction was done by injection of ferrosilicon and/or aluminium powder through the slag door into the molten slag. In an industrial process the most preferred method is to charge hot BOF-slag into the furnace and the pre-reduction step will be done by injection of carbon reductants into the molten slag. This was also simulated and tested by first melting the steel slag without addition of a reducing agent and then a reduction as described above.

Most of the iron, phosphorus and vanadium were successfully recovered in the metal phase. The recovery is 92-99% for Fe, 96-99% for P, 70-92% for Cr, 50-96% for Mn and up to 99% for V. These results demonstrate the high reducing efficiency of this



During injection Test set-up

Figure 6: Experimental setup of the pilot trials using a 5 MVA EAF[3, 4]

process concept. The final V-content in some typical reduced slag obtained is shown in Table 3. The suitability of the water granulated reduced slag for use as slag cement was also tested. The performed tests have shown excellent results compared to the use of GBFS (Granulated Blast Furnace Slag).

Table 3: Chemical composition of some of the typical slag samples from the AC-furnace trials

	%Fe	%V	%CaO	%SiO_2	%MnO	%P_2O_5	%Al_2O_3	%MgO
Slag 1	0.08	0.03	41.6	37.4	0.32	0.01	2.9	17.2
Slag 2	0.07	0.03	37.6	14.2	0.21	0.01	37.9	11.2
Slag 3	0.64	0.04	37.2	23.5	0.34	0.01	27.9	11.9

To summarise, the slag reduction using an AC-furnace has shown that a high reduction degree could be achieved in a controlled way. Pre-reduction using coal combined with final reduction using stronger reductants, such as FeSi or Al, seems to be a promising and cost effective way to achieve high vanadium recovery and to make a good slag product.

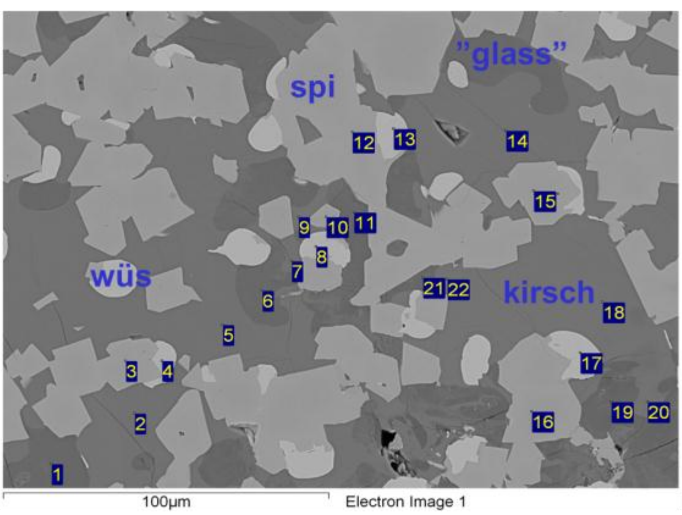
Enrichment of vanadium[5]

As the cost of processing one tonne of slag is more or less the same, the process cost per unit of recovered vanadium will thus be decreased almost proportionally with increased V-content in the slag. For instance, if the vanadium content in the steel slag has been enriched two-fold, the cost to recover one kg of vanadium will be about 50% less. Due to this, a new way to enrich vanadium in the slag by a two-step blowing process has been developed by SSAB EMEA in the VILD-project. The process is in principle the same as the MURC- process, which is widely practised in the Japanese steel plants for peroxidation and removal of phosphorus. The only difference is that in the VILD-process we also pre-oxidise vanadium and by that produce a pre-blown slag with a basicity of around 1.5 and with a vanadium content

of about the double of a normal SSAB BOF-slag. Over 85% vanadium could be captured in the pre-blown slag. By this procedure, the vanadium content could be enriched to more than 5% as compared to 2-3% V in a normal BOF-slag. This slag is called LUVA-slag (the **LU**leå **VA**nadium slag). It could be sold for external V_2O_5 production and/or used as feed material for the slag reduction process developed in the IPBM- and the VILD-project.

Further enrichment of vanadium of the LUVA-slag has also been investigated as vanadium in the LUVA-slag is existing in the $(Fe,Mn)O{\cdot}V_2O_3$ spinel phase as shown in Figure 7. If the spinel phase could be successfully separated, it will have great economic potential, as the spinel phase does not contain any phosphorus as indicated in Figure 7. This means that it can be used as pure V-source for direct FeV production without the need to go via the expensive V_2O_5 step.

Metallurgical manipulation of the conventional BOF-slag to concentrate vanadium into some targeted phases has also been studied in the VILD project. Figure 8 shows the results from a test where vanadium was concentrated into the solid solution of the $3CaO{\cdot}V_2O_5$-$3CaO{\cdot}P_2O_5$-$2CaO{\cdot}SiO_2$ system[6]. The grey coloured phases, marked as "9" and "10" in Figure 8, have a V_2O_5-content of up to 30-33%. The main challenge for this method is how to control the cooling rate on an industrial scale and by that, generating large crystals of the V-enriched phase, which again will make it possible to be separated from the rest.



	MgO	Al2O3	SiO2	P2O5	CaO	TiO2	V2O5	Cr2O3	MnO	FeO	Total
spinel	0.7	0.6	0.2	0.0	0.5	4.5	34.9	15.3	10.9	38.0	105.6
kirschteinite	1.3	0.1	33.8	0.4	34.2	0.6	0.5	0.2	11.6	18.4	101.1
"glass"	0.3	0.1	31.2	5.4	52.1	0.2	1.3	0.3	4.2	5.8	100.8
wüstite	0.8	0.1	0.3	0.0	0.5	0.3	1.6	0.3	15.6	80.5	100.1

Figure 7: Phase analysis of a two-step oxidation slag

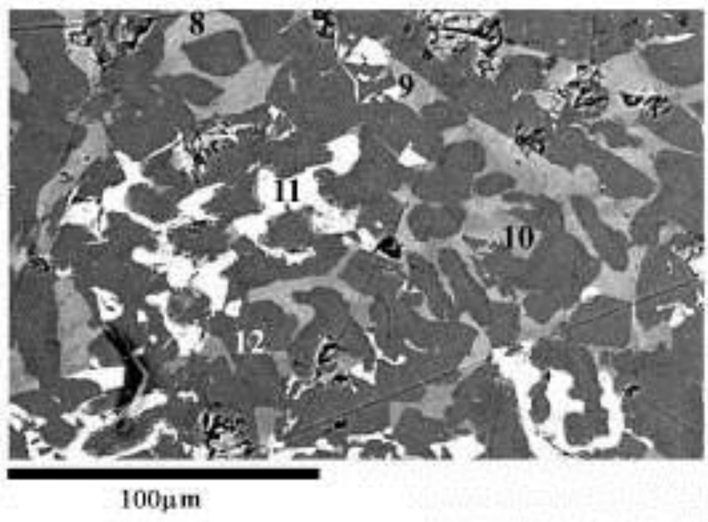
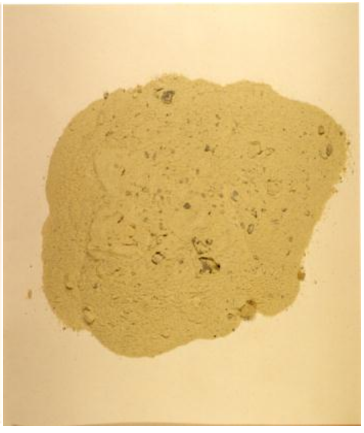


Figure 8: Modified BOF-slag and the V-concentrated phases

Recovery of Fe, P and Mn from Conventional BOF-slag

Conventional BOF-slag with low vanadium content has also been tested in the IPBM-process where Fe, P and Mn are recovered into the metal phase while the slag is modified to three various products, i.e. (1) hydraulic powder by total reduction and water granulation, (2) metallurgical powder by deep reduction and addition of lean quality alumina, (3) cement clinker by partial reduction of the slag. Details of the results have been reported elsewhere[1]. Two of the products are shown in Figure 9. This was recently verified and pilot tested again for an international company.

Water granulated glassy slag



Calcium aluminate powder

Figure 9: Water granulation unit for slag granulation and two slag product samples

Recovery of Ni, Cr and Other Valuables from Slag, Fine Grained Wastes from Stainless Steel Production

The ETEUSCE-project

The same IPBM-concept was also applied in the ETEUSCE-project[7], which was a research project financed by the BriteEuRam during 1998-2000. ETEUSCE stands for Economical, Technical and Ecological Utilisation of treated steel Slag in Civil Engineering of high demands. The same DC-furnace was used for recovery of Ni and Cr from slag and residues from stainless steel production. A stoichiometric mixture of fine grained residues, like dust, millscale, pickling sludge *etc*., generated from a stainless steel producer in Sweden was mixed and co-processed with EAF and AOD-slag from the same steel plant. The Cr-level in the reduced slag could be controlled to 0.04%, which allows it to be used in cement and other construction industry. A metal with 15-20% Cr and 4-5% Ni was obtained. The Ni-recovery yield is over 99% and Cr-recovery generally over 90%.

Use of pickling sludge as slag former to AOD for recovery of Ni, Cr and CaF_2

Pickling sludge is a hazardous residue generated at stainless steel plant during the neutralisation of the pickling solution. In order to reuse the solution, the excess concentration of metal ions has to be removed. To achieve this, $Ca(OH)_2$ is added in the neutralisation plant to adjust the pH-value. As a result of this, a sludge, called pickling sludge, with high content of CaF_2 and metal hydroxides is formed and precipitated. The slurry and the cake after pressure filtration of the slurry are shown in Figure 10. Typical dried pickling sludge contains about 40-50% CaF_2, 5-30% $Ca(OH)_2$, 20-30% $Fe(OH)_3$, 5-9% $Cr(OH)_3$, 2-4% $Ni(OH)_2$ and 2-4% SiO_2. The handling of a dried pickling sludge is problematic as it easily pulverises and becomes a fine powder.

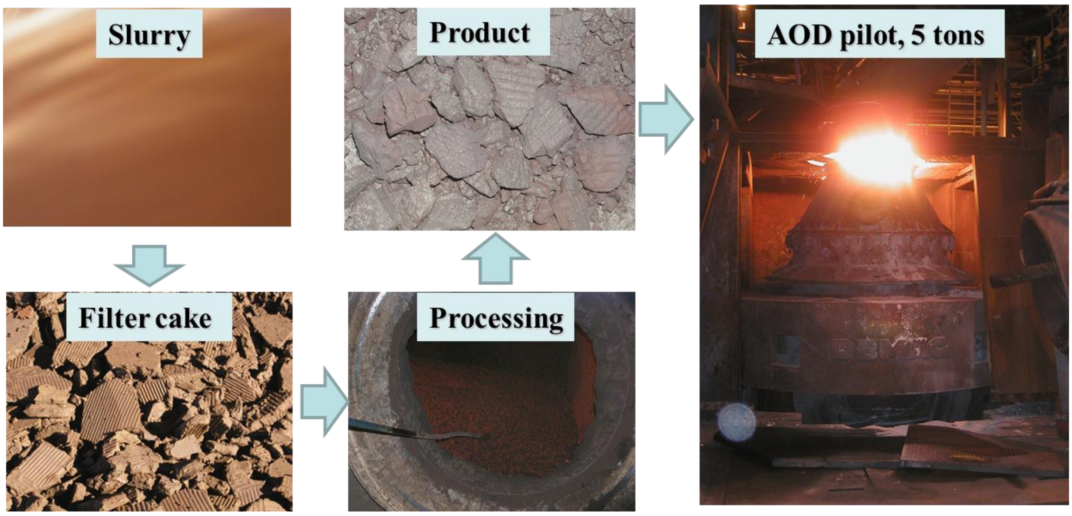


Figure 10: Processing of pickling sludge for use as a slag former in AOD

A method for thermal treatment of the filter cake for metal and CaF_2 recovery has been invented and developed by Outokumpu Stainless and Swerea MEFOS[8,9]. The invented method was pilot tested using large scale furnaces at Swerea MEFOS. After the treatment the material became dark and strong. The product, called Hydrofluss, consists mainly of CaF_2, Cr-, Mo- and Ni-oxides. It is a perfect substitute for the fluorspar used in the AOD-process.

Use of the Hydrofluss as a slag former in AOD-process was simulated and tested using the 5 tonne universal converter at Swerea MEFOS in a test campaign with a duration of one week. The behaviour of the material was properly tested and studied. No difference compared to the reference trials could be observed. In addition to the saving of a large quantity of fluorspar, all valuables such as Ni, Mo and Cr in the calcined sludge were efficiently recovered to the metal phase during the reduction step. Fluorspar is in fact classified as a critical raw material in the EU.

The Hydrofluss concept has shown that simple thermal treatment could solve the problem of a complex residue material, and turn a hazardous waste into a valuable product. By doing this the steel plant not only saves a large amount of fluorspar, but also Ni, Mo and Cr, while avoiding high landfilling costs. The concept has been established and utilised in the steel plant after the pilot testing at Swerea MEFOS and long term full scale trials in the steel plant.

Recovery of Zn, Ni, Co, Mo, V and other valuables from other residues

Due to the special features and characteristics of a DC arc furnace, such as high thermal efficiency, rapid response time, higher metal yield and capability to treat fines *etc*., a wide range of applications of the DC-furnace technology for upgrading secondary materials have been developed and pilot tested at Swerea MEFOS in the last decades. In addition to the applications mentioned previously, the following processing technologies have also been developed at Swerea MEFOS using the same DC furnace:

- Recovery of Zn and Pb from carbon steel EAF-dust;
- Recovery of Ni, Cr and Mo from EAF dust, millscale and other residues from the production of stainless steel;
- The AshArc process developed by ABB in the 1990s where incinerator ashes were processed in the DC-furnace. The ashes were transformed into an inert glassy slag product and a fume fraction where the alkalis and other volatile metals are efficiently enriched;

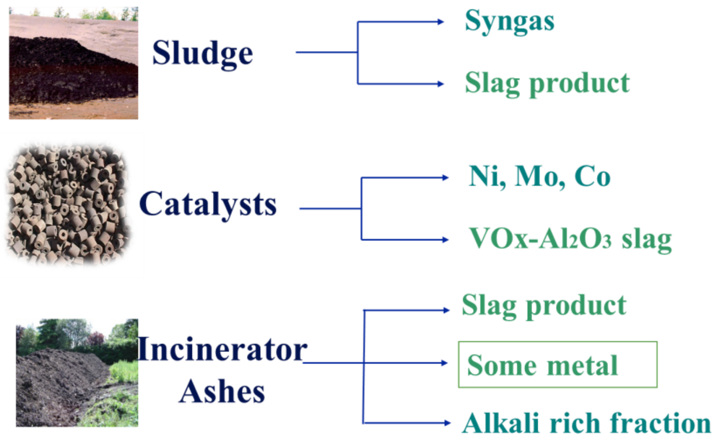


Figure 11: Some examples of DC arc furnace applications for metal recovery

- The catalyst treatment process where Ni, Co, Mo in the spent catalysts are recovered in a metal phase, whereas vanadium oxide is enriched and collected in a slag phase (up to 20-30% vanadium oxide);
- The Mn-sludge upgrading process where sludge from Mn-processes was treated for alkali-removal and a clean Mn-slag product was obtained for reuse as raw material[10];
- Treatment of dust from FeNi smelter for high Ni-recovery

Some of these applications are illustrated in Figure 11.

Conclusion

The extensive pilot experience of Swerea MEFOS has shown that there is a wide range of options for economic and ecological recovery of metals, minerals and energy from metallurgical slags. The VILD-project alone has a potential of savings of more than 1 million tonnes CO_2 every year for a steel producer in Sweden and Finland, while the metal value alone corresponds to more than 150 million US$ each year. The successes of the projects like VILD, Hydrofluss and metal recovery from catalysts *etc*. have demonstrated that through technological innovation it is still possible to make money from industrial residues. Pilot testing is one of the most important keys for the development of technology know-how and innovation. The experiences from the IPBM-project have shown that the metal recovery and diversity of the slag products are the key issues for the future slag utilisation to meet the ever increasing demands of the mechanical and environmental properties of the slag products and the ever increasing raw material prices. Post-furnace treatment of molten slag for metal recovery, control of the slag chemistry and mineralogy will most likely be a necessity for the metal producers and smelters in the near future.

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