Abstract: Slag is a byproduct generated during metal production and huge amounts of various slags are produced yearly in the world. The annual amount of generated steelmaking slags alone is more than 100 million tons. Fully utilization of this huge amount of byproduct is limited by its leaching and volume stability properties. In the recent years Swerea MEFOS have been involved a large number of projects aiming for increased slag utilization. These projects included slag stabilization 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.

The major results from the following projects will be highlighted and described in this paper:

- IPBM, In-Plant Byproduct Melting process
- ViLD – Vanadium recovery from LD-slag, an ongoing eight-years slag reduction project in Sweden and Finland
- Converting of pickling sludge into a valuable slag former for the AOD-process
- Dry and wet granulation of metallurgical slags

The pilot equipment used for these development works include a 3 MW DC-furnace, a 5 MVA AC-furnace, a 5-tons converter, and various granulation facilities. This paper will also show some tests performed in industrial scale.

The extensive pilot experiences of Swerea MEFOS have shown that there is a wide range of options for economic and ecological recovery of metals, minerals and energy from hot metallurgical slag.

Keywords: Slag, treatment, reduction, metal and heat recovery, granulation, slag product

1. Introduction

The metallurgical industry generates every year huge amounts of slag. The annual amount of generated steelmaking slags alone is more than 100 million tons. The steel slag is normally used as construction materials, for instance, for road and river bank construction. Fully utilization of this huge amount of byproduct is limited by its leaching and volume stability properties. In addition to the useful minerals in the slag, there is also a considerable amount of feasible heat loss in the hot slag. For FeNi-production for instance, more than 90% of all input electric energy in the smelting is reported to the slag phase and lost. The heat content in one ton hot molten slag at 1400-1600 °C is about 500-600 kWh. This means that if we could recover 50% of the feasible heat from the 100 million tons of molten steel slag, we will recover 20-30 TWh heat from the steel slag alone. If the slag could be used for cement production, it will be further saving huge amounts of CO₂ emission as most of the steel slag contains 40-50% CaO. By using steel slag the energy and CO₂-intensive calcination of limestone could be avoided. For production of one ton calcined CaO the emission of
CO₂ is about 1.6 tons and energy consumption almost 2 MWh. Swerea MEFOS have in the recent 20 years participated in a large number of projects aiming for increased slag utilization. These projects included slag stabilization 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. Some of these projects will be highlighted in this paper.

2. Slag reduction and modification

2.1 The IPBM-process [1, 2]

The IPBM-process stands for In-Plant Byproduct Melting Process. It is a process that has been initiated by Swerea MEFOS and developed together with CRM and FEhS some 15 years ago. The basic concept is well illustrated in Figure 1.

![Fig. 1 The IPBM-process using a DC-furnace with hollow electrode](image)

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, melts and reacts immediately. The valuable elements are concentrated in the metal phase and the rest of the reduced slag is modified accordingly to the target compositions. The more volatile elements, like zinc, lead cadmium, alkalis and halogens in the dust, will be evaporated and be collected in the filter system.

The treated materials include various steel slags, EAF dust, millscale, pickling sludge, oily millscale from both carbon steel and stainless steel production. In the followings some of the examples will be highlighted.

2.1.1 Treatment of BOF-slag for vanadium recovery
The Swedish BOF slag consists of 44% CaO, 10% SiO₂, 11% MgO, 25% FeO, 4% MnO and 5% V₂O₅. The vanadium balance of the SSAB steel plants is illustrated in Figure 2. The LKAB pellets used in the ironmaking process contains about 0.1% V. This will end up in the hot metal in the blast furnace. The hot metal will contain about 0.3% V. During BOF-process the vanadium will be oxidised and end up in the BOF-slag. After crushing, the coarser fraction, about 50% of the BOF-slag, is recycled to the blast furnace for further use of CaO in the slag. The finer fraction is temporarily landfilled within the steel plant for future use.

In order to recover the vanadium from the slag and make the slag usable, reduction trials based on the IPBM-concept were carried out at Swerea MEFOS using a 3 MW DC-furnace with hollow electrode. Several weeklong test campaigns have been conducted for recovery of vanadium from the slag. It is shown in the study that over 90% of the vanadium recovery could be achieved and the slag could be composed to three different slag products with target slag composition:

- cement clinker material (by partial reduction)
- hydraulic binder (CaO/SiO₂=1, by addition of sand)
- metallurgical powder for desulphurization (by addition of Al₂O₃)

Overall more than 100 tons of BOF-slag has been treated. The pilot tests have proved that the DC-furnace is a powerful reduction tool for recovery of vanadium from the BOF-slag. The reduction degree and slag composition were easily controlled by the carbon/slag ratio and the addition of slag formers. The carbon/slag rate is about 130 kg per ton slag and the energy consumption is about 1.3 MWh/ton slag. About 220 kg metal with up to 10-12% vanadium and 4% Mn could be obtained and about 800-1000 kg clean slag will be formed depending on the target slag composition.

2.1.2 Treatment of BOF-slag with low vanadium content

Most of BOF-slag in the world has low vanadium content, therefore the IPBM-process has also treated BOF-slag from other countries which has higher content of phosphorus but much lower content of vanadium. Table 2 shows a summary of slag products that have been produced during one of the test campaigns, based on low vanadium BOF-slag. The chemical composition of the obtained slag products is compared with the target slag composition. It is clearly shown that it is relatively easy to control the reduction degree and the chemical composition of the slag.
Table 1 Slag composition from reduction of low vanadium BOF-slag

<table>
<thead>
<tr>
<th>Test no</th>
<th>Product</th>
<th>Slag modifier</th>
<th>Target From test</th>
<th>Fe</th>
<th>CaO</th>
<th>SiO₂</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Cr₂O₃</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>Clinker material</td>
<td>Sand, Bauxite</td>
<td></td>
<td>3.7</td>
<td>62-66</td>
<td>20-21</td>
<td>3.5</td>
<td>2.2</td>
<td>4.7</td>
<td>&lt;5</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>Metallurgical powder</td>
<td>Bauxite</td>
<td>Target From test</td>
<td>4-3</td>
<td>54.7</td>
<td>20.8</td>
<td>1.8</td>
<td>21.9</td>
<td>6.9</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Metallurgical powder</td>
<td>Bauxite</td>
<td>Target From test</td>
<td>&lt;2</td>
<td>50-55</td>
<td>16</td>
<td>1.18</td>
<td>0.2</td>
<td>2.2</td>
<td>2.10</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Hydraulic binder</td>
<td>Scrap residue</td>
<td>Target From test</td>
<td>0.35</td>
<td>56.6</td>
<td>19.6</td>
<td>1.18</td>
<td>0.2</td>
<td>22</td>
<td>2.85</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Hydraulic binder</td>
<td>Scrap residue</td>
<td>Target From test</td>
<td>&lt;2</td>
<td>50-55</td>
<td>16</td>
<td>1.18</td>
<td>0.2</td>
<td>2.2</td>
<td>2.10</td>
<td></td>
</tr>
</tbody>
</table>

- BOF-slag analysis - - - 18.4 51.0 11.3 3.67 2.56 1.60 1.20 -

Figure 3 shows the water granulation unit used for the hydraulic binder production and two of the slag products obtained from the test campaign; one is water granulated slag aiming for use as hydraulic binder and the other one is a calcium aluminate product, called metallurgical powder, aiming for use as desulfurization agent in secondary metallurgy. As the slag is well reduced, the calcium aluminate slag was white and disintegrated into powder during cooling.

![Fig. 3 Water granulation unit for slag granulation and two slag product samples from one of test campaigns](a) Water granulator (b) Water granulated glassy slag (c) Metallurgical powder, calcium aluminate product

2.1.3 Treatment of EAF slag and EAF dust from stainless steelmaking for Cr-, Ni- and Zn-recovery

The same IPBM-concept was also applied in the ETEUSCE-project 1, 3 which was a research project financed by the Brite EuRam during 1998-2000. ETEUSCE stands for Economical, Technical and Ecological Utilization of treated steel Slag in Civil Engineering of high demands. The participating partners included Swerea MEFOS from Sweden, FEhS from Germany, CRM from Belgium and 10 other industrial partners. The slag treatment of stainless steel slags was continued in this project. The same IPBM furnace was used for recovery of Ni and Cr from EAF dust and slag from stainless steelmaking. The Cr-level in the reduced slag could be controlled to very low level, which allows it to be used in cement and other construction industry. The Ni-recovery yield is over 99% and Cr-recovery generally over 90%. The energy consumption was about 1.5 MWh/ton EAF dust. From one ton EAF dust, about 500 kg metal with 15-20% Cr and 4-5% Ni could be obtained. The slag amount is low, 300-400 kg per ton dust.
There are industrial plants for EAF-dust treatment in Europe based on this principle. The furnace capacity is 3-9 MW. For treatment of EAF and AOD slags the Cr-content will be removed to an extremely low level. In our pilot plant trials, the lowest Cr-content in the slag achieved is 0.02%. The Cr-leaching problem is thus solved and the slag could also be composed to a defined composition.

2.2 ViLD-project for vanadium recovery [4, 5, 6]

ViLD stands for Vanadium in LD-slag (=BOF-slag), which it is an eight-years research program financed by MISTRA (Foundation of Strategic Environmental Research in Sweden) and the Nordic steel and mining industries. This research program is a continuation of the vanadium recovery project that has been initiated in the IPBM project. The ViLD-concept is aiming at converting of the currently disposed BOF-slag into two different products; a V-product and a low vanadium slag product. The aim is also to optimize the process choice based on the technically, economically and ecologically most feasible technique. The R&D activities of the ViLD-project are summarized and illustrated in Figure 4.

As shown in the figure the most important issues that have been heavily investigated in this project are:
- V-enrichment to further increase the V-content in the slag by modification of the existing production procedure and control of mineral composition of the slag
- V-P separation to avoid the V₂O₅ route aiming for direct FeV-making
- Economically and technically optimize the slag reduction step aiming for highest possible vanadium recovery and at least a clean slag product
- Diversification of the final and intermediate V-products and process routes including direct use of the intermediate FeV product with 10% V and 1% P as alloying agent
- Increased co-operation with potential users of the V-products from ViLD-concept

Fig. 4 Research activities of ViLD-project
Some of the extensive test works on slag reduction are highlighted in the followings.

2.2.1 Optimization of slag reduction

The major cost of the vanadium recovery process is located in the slag reduction step. Therefore extensive work has been carried out to find the most efficient and economical way to extract vanadium from the slag. The reduction work includes extensive modeling works using FACTSage and HSC Software to evaluate the different approaches of slag reduction including selective reduction and total reduction. Reductions with C, FeSi, Al and CaC₂ were simulated. Also carbon in combination with FeSi, Al and CaC₂ as reductants has been calculated. Based on the calculated results, it was decided to focus the test works on direct hot slag reduction using FeSi, combined carbothermic reduction of iron with final reduction using FeSi and Al using an AC- or DC-furnace. Reduction of V-enrich slag has been tested in several test campaigns. The test works in pilot and industrial scale are summarized in the followings and in Figure 5:
- Hot slag reduction during tapping using FeSi and Al (4 tons industrial tests)
- Hot slag reduction in a slag ladle by injection of FeSi powder (4 tons of slag in pilot trials and 10 tons in industrial scale trials)
- Hot slag reduction using a KALDO-furnace (2 tons of slag in pilot scale)
- Hot slag reduction using a 5 MVA AC-furnace (pilot)
- Reduction of cold LD-slag using a 3 MW DC-furnace (pilot)
- Reduction of cold slag of V-enriched slag using the same DC-furnace

All pilot tests were performed at Swerea MEFOS and all industrial trials at SSAB EMEA Luleå works.
Direct hot slag reduction using FeSi during tapping if successful is a simple and easy concept. As silicothermic reduction of the LD-slag is strongly exothermic no external heat is needed. In fact the reaction has to be cooled as slag reaction could be quite intensive and slag temperature could easily be raised to over 1700 °C. One of the major challenges with this method is the control of the reaction and thus also the process temperature. The other big challenge is the Si-efficiency as FeSi is an expensive reductant.

Figure 6a shows the hot slag in the slag ladle just after a trial. On the top the unreacted additives could be seen. The slag was hot. After cooling, the slag ladle was set upside down to strip the obtained metal and slag. The well separated slag and metal pieces from one of the trials is shown in Figure 6b. Preliminary analysis of slag samples has indicated that the V-content in the slag could be reduced to a low level. SEM-analysis of metals shows that the V-content is about 8%, which indicated a quite good slag reduction.

In order to achieve a better control of vanadium recovery and process temperature, slag reduction test activity was continued using an AC-furnace. Figure 7 shows the experimental set-up for slag reduction trials using a 10 tons AC-furnace at Swerea MEFOS [5, 7]. By this set-up slag could be added in solid or molten state and the injection possibility of reducing agent or fine materials was also possible. Table 2 shows some of the test results from the AC-furnace trials. As shown in the table, the slag is well reduced and the V-content could be reduced to below 0.1% meaning that it should be possible for use for cement production. The V-recovery yield was for most cases over 90% and for the highest more
than 99% has been achieved. This is extremely important as the processing cost was thought to be covered by the potential income of the recovered vanadium value and the reduced slag should have a V-content below 0.1% for use in cement industry.

The tests of the water granulated reduced slag have shown that the slag product is suitable for use in cement production.

![Diagram of slag reduction trials](image)

**Fig. 7 Experimental set-up for slag reduction trials using a 10 tons AC-furnace**

<table>
<thead>
<tr>
<th>Test</th>
<th>Fe</th>
<th>V</th>
<th>CaO</th>
<th>SiO₂</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Cr₂O₃</th>
<th>V-yield (%)</th>
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<td>0.02</td>
<td>26.5</td>
<td>15.16</td>
<td>0.01</td>
<td>99.3</td>
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<td>0.06</td>
<td>42</td>
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<td>0.21</td>
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<td>32.8</td>
<td>1.23</td>
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<td>9.48</td>
<td>14.72</td>
<td>0.02</td>
<td>90.6</td>
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<td>0.22</td>
<td>38.7</td>
<td>34.1</td>
<td>1.35</td>
<td>0.02</td>
<td>9.73</td>
<td>15.01</td>
<td>0.02</td>
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<td>0.05</td>
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<td>0.03</td>
<td>37.6</td>
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<td>17.47</td>
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<td>1.42</td>
<td>0.00</td>
<td>15.23</td>
<td>16.74</td>
<td>0.02</td>
<td>97.8</td>
</tr>
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</table>

### 2.3 The slag products

Two major slag products have been considered and made during the various slag reduction trials; one is granulated glassy slag for cement use and the second one high Al₂O₃ calcium silicate slag also aiming for cement use. Figure 8 shows one of the obtained high Al₂O₃ calcium silicate slag product. As shown, it is white meaning it has been well reduced.
Two of the water granulated reduced slag samples aiming for cement use were tested for its hydraulic properties. One is from AC-furnace reduction and the other from DC-furnace reduction. The granulated slag samples were crushed, grounded and mixed with OPC. The strength of these was measured after 2, 28 and 91 days and compared with a reference sample which was consisted of standard slag product of SSAB MEROX, MERIT5000 mixed with OPC. Table 3 shows the test results as compared with the reference mixture. It is clearly shown that the water granulated VİLD-slag product has the same hydraulic property as MERIT5000.

Table 3 Physical properties of the obtained VİLD slag products compared with the reference MERIT5000/OPC

<table>
<thead>
<tr>
<th></th>
<th>AC-slag sample</th>
<th>DC-slag sample</th>
<th>Reference Merit5000/OPC</th>
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</thead>
<tbody>
<tr>
<td>Strength, MPa</td>
<td>12.8</td>
<td>15.6</td>
<td>16.5</td>
</tr>
<tr>
<td>After 2 days</td>
<td>43.6</td>
<td>54.4</td>
<td>52.2</td>
</tr>
<tr>
<td>After 28 days</td>
<td>56.7</td>
<td>60.2</td>
<td>61.0</td>
</tr>
<tr>
<td>After 91 days</td>
<td>73.2</td>
<td>97.3</td>
<td>99</td>
</tr>
<tr>
<td>Glass content</td>
<td>3018</td>
<td>2961</td>
<td>2924</td>
</tr>
<tr>
<td>Density, kg/m³</td>
<td>460</td>
<td>466</td>
<td>505</td>
</tr>
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</table>

3. Converting pickling sludge to a slag former for AOD

Pickling sludge is a hazardous residue generated at stainless steel plant during neutralization of 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 neutralization plant to adjust the pH-value. As a result of this a sludge, called pickling sludge with high content of CaF₂ and metal hydroxides, is formed and precipitated. The sludge and the cake after pressure filtration of the slurry are shown in Figure 9. Typical dried pickling sludge contains about 40-50% CaF₂, 5-30% Ca(OH)₂, 20-30% Fe(OH)₃, 5-9% Cr(OH)₃, 2-4% Ni(OH)₂ and 2-4% SiO₂. Handling of a dried material of this is problematic as it easily pulverises and becomes a fine powder.

A thermal treatment process of the filter cake 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 CaF₂, 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 ton universal converter at Swerea MEFOS in a weeklong test campaign. 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, a large amount of valuables such as Ni, Mo and Cr was efficiently recovered to the metal phase.

![Image](image_url)

Fig. 9 Processing of pickling sludge for use as a slag former on AOD

The Hydrofluss-concept has shown that simple thermal treatment could solve problem of a complex residue material, and turn a hazardous waste into a valuable product. By doing this the steel plant saves, in one hand, a large amount of fluorspar, Ni, Mo and Cr and in the other hand, the high dumping cost. The concept has been established and utilized in the steel plant after the pilot testing at Swerea MEFOS and long term full scale trials in the industry.

4. Slag granulation for energy and material recovery

Since 2005, Swerea MEFOS has been involved in development of dry granulation of metallurgical slag. Dry granulation has several potential advantages compared to water granulation [10]:
- Lower investment cost
- Decreased use of water
- Increased possibility for energy recovery
- Decreased risk for possible formation of hazardous gases, such as HF, SO2 and H2S
- Easier recovery of the metal fraction in the slag

The investigations performed at Swerea MEFOS included control of the physical and chemical properties of the slag granulates. Several methods have been tested. Figure 10 shows one the experimental set-ups aiming for gas granulation of stainless steel slags for control of leaching and physical properties.

An induction furnace for melting of the test slags is connected to the granulation facilities. The furnace has a capacity for 30-40 kg slag. Once the slag is melted and the target temperature is reached, the furnace was tilted and the liquid
slag was tapped into the pre-heated slag box. Nitrogen gas was injected through a split 200 mm underneath the tap-hole of the slag box. A portable Testoterm instrument was used for gas and temperature measurements. The granulated slag was collected from the sample boxes (1-10), granulates was to some extent classified according to their size and weight; hence finer fractions in the boxes closest to the gas off-take. Figure 11 shows the granulated slag from one of the trials.

The performed tests included testing of particle size, shape uniformity, density, strength and leaching properties of the obtained granulates by varying various operation parameters like slag chemistry, gas flow, pressure, slag temperature etc. There is also a rotating disc test facility at Swerea MEFOS which could be connected to the induction furnace. All slag granulation equipment at Swerea MEFOS are portable and can also be sent to the metallurgical plants for in-situ testing of industrial slag.
Also the granulation gas temperature was measured during the trials. It has been shown that very high gas temperature could be reached by gas granulation. The thermal energy in one ton molten slag at 1400-1600 °C is about 500-600 kWh. Considering that every year about 100 million tons of steel slag is produced, if 50% of the heat is recovered, this will correspond to 20-30 TWh for the steel industry alone. Swerea MEFOS recently awarded a national research program by the Swedish Energy Agency aiming for heat recovery from metallurgical slags based gas granulation technology. This project will start this year.

5. Conclusions

The extensive pilot experiences of Swerea MEFOS have shown that there is a wide range of options for economic and ecological recovery of metals, minerals and energy from hot metallurgical slag. The ViLD-project alone has a potential of saving over 1 million tons CO₂ every year for a steel producer in Sweden and the metal values alone corresponds to over 100 million € each year.

The successes of the ViLD- and Hydrofluss-projects have demonstrated that by technology 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. It is believed that the diversity of the slag products will be the key issue for the future slag utilization to meet the ever increasing demands of the mechanic and environmental properties of the slag products. To enable this, possibility of post furnace treatment of molten slag for control of the chemistry and mineralogy will be an important tool and probably a necessity for the metallurgical smelters in the near future.

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