SALT EXTRACTION PROCESS-A NOVEL ROUTE FOR METAL EXTRACTION FOR CHROMIUM RECOVERY FROM SLAGS AND LOW-GRADE CHROMITE ORES

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ABSTRACT

In this work, a novel salt extraction process route is put forward towards metal extraction from slag, low-grade ores and other oxidic materials such as spent refractories using molten salts at a temperature range between 800ºC ~ 950ºC. This part focuses on the recovery of metal values, primarily Cr and Fe, from EAF slag and chromite ore. The impact of different factors to the dissolution of slag, such as temperature, holding time, flux content and weight ratio of flux/slag were studied. Based on the optimized experimental factors, the salt bath containing metal values recovered from the slag/ore was electrolyzed under an applied voltage of 2.8V. The cathode deposit was subjected to SEM/EDS and XRD analyses and were confirmed the formation of CrFe alloy. The process was also extended for production of CrFe alloy directly from chromite. Preliminary results obtained so far are positive with respect to the feasibility of this method.

INTRODUCTION

During the production of alloy steel, many metals such as Cr, Mo, V, Ti, etc., get oxidized and end up in the slag or dust. Apart from the energy and metal losses, these slags pose a serious environmental threat as these metals finally end up in slag dumps only to be leached by acid rains over years. Thus, it is imperative to recover the metals before the slags can be used as land fills or even for road making. The recovery of these metals from slags, also offer an economic added advantage. In this context, a process that can be used both for slags containing these metals as well as low grade ores would be attractive as the high grade ore availability is shrinking on a global perspective. Traditionally, the recovering processes of metals can be classified into three categories: pyrometallurgy, hydrometallurgy, solvent extraction and ion-exchange [7]. By applying mineral processing technologies, such as crushing, grinding, magnetic separation, eddy current separation, flotation and so on, leaching or roasting, it is possible to recover metals such as Fe, Cr, Cu, Al, Pb, Zn, Co, Ni, Nb, Ta, Au, and Ag etc. [3]. Particularly, EAF stainless steel slags contain high content of Cr. Some laboratory investigations have been performed on carbon reduction of iron and chromium oxides [1, 2, 4] in EAF slag. A carbon saturated Fe-C melt or iron carbide can be obtained, and only when a certain number of Fe-C droplets are formed, reduction of Cr_2O_3 starts to form a Fe-Cr-C alloy. Reduction of chromium by iron melts [5] or simultaneous reduction of Cr_2O_3, MnO, FeO and SiO_2 in EAF slag [6] by aluminum at 1793K has also been investigated. Further, recovery of Cr, Ni and Fe from dust by carbon has been reported [9]. However, these processes are carried out at very high temperatures and it is difficult to obtain the metal with high purity.

The current research is focused on an electrolytic process for extraction of metal values in molten salt systems, which is called Salt Extraction Process proposed by the present authors [8]. Actually, this process is not limited for extraction of chromium, it also shows a potential to extract Fe, Mo, V, Ti, etc. In this paper, the results of the laboratory scale investigations of extraction of FeCr alloy from industrial EAF slag and chromite ore are presented.

METHDOLOGY

This new process is based on the principle of leaching of the metal values from the materials covering slags, low grade ores and oxidic refractory waste materials using molten salts at temperature above 600ºC. It can be divided into two steps: First, the slag or the ore containing Cr is dissolved into the molten salt phase at a suitable temperature. This extraction step is enabled by the choice of a suitable fluxing agent. Earlier work in the present laboratory has shown $AlCl_3$, which has now been protected by a patent application, is a powerful fluxing agent. Secondly, the salt phase is subjected to electrolysis in order to recover the metal of interest as a cathode deposit. The schematic diagram of this process is shown in Figure 1. Apart from the consumption of $AlCl_3$ flux, it is interesting to note that the salt melt used for extraction can be recycled. There is also the option of aqueous processing of the salt phase containing the metal values. The process can designed to be continuous by combining the two steps. The anode off-gas from electrolysis, Cl_2 can be reused for accentuating the dissolution of slag/ores. The residue after processing, which consists essentially of Al_2O_3 and SiO_2, can safely be used for landfill, building construction or as a raw material for the refractory industry.

In the present work, investigations were carried out in order to optimize the process parameters for dissolution of slag/chromite in the eutectic salt mixtures of NaCl-KCl containing $AlCl_3$ flux. Based on the optimized conditions, lab-scale investigations of electrolysis were carried out applying a cell voltage of 2.8V. Ferrochrome was recovered as the cathode deposit.

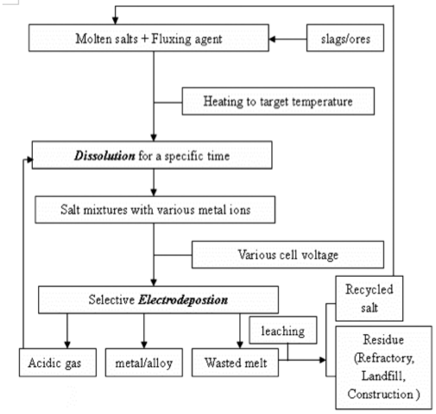


Figure 1: Schematic diagram of salt extraction process

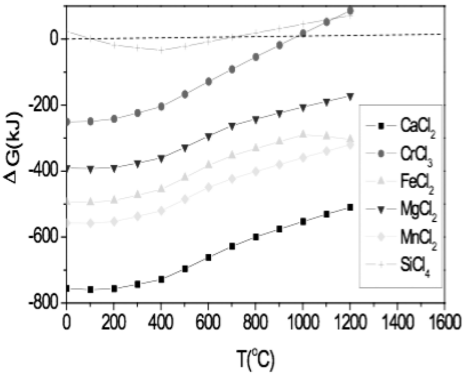


Figure 2: The standard Gibbs energy change of different metal chlorides

Materials and Experiments

Salt Extraction Step

Two slag samples from EAF practices at Uddeholm Tooling AB were investigated in the present work. The chromite ore powder was of Vietnamese source. The chemical compositions of the raw materials are shown in Table 1. The salts, NaCl and KCl (99.5%, E.Merck, Darmstadt, Germany), slag, chromite ore, and the alumina crucible (99.5%, 40 mmOD, 36 mmID, 60 mm height from KERANOVA AB, Sweden) were dried under 400°C for at least 24 hours and stored in an oven at 110°C. The flux used, $AlCl_3$, was supplied by E.Merck, Darmstadt, Germany. The salt mixtures NaCl-KCl, flux and EAF slag/chromite were mixed evenly, heated to the target temperature, and held for a fixed time with a lid. Argon gas (ICP 5.0, AGA gas AB, Sweden) was introduced as the protective gas. The gas was cleaned from moisture impurity by passing through silica gel. The crucible was crushed to collect all the substances after dissolution. For slag No. S1, each salt melt was completely dissolved in distilled water. The residue was prepared for chemical analysis. The filtrate was used for ICP-AES analysis(Varian Vista AX). For slag No. S2, in view of the high content of Cr_2O_3, only a small amount of each salt melt was sampled, and dissolved in distilled water as $CrCl_3$ has a low solubility in water.

Table 1: Composition of EAF slags from Uddeholm Tooling AB and Vietnamese chromite

No.	CaO	MgO	Al_2O_3	SiO_2	FeO	MnO	Cr_2O_3	MoO
No. S1	41.4	7.91	3.29	10.44	23.06	4.98	3.25	0.17
No. S2	29	12.4	3.6	18.4	11.2	2.5	21.1	0.02
No. C1	0.12	8.88	11.94	12.73	22.31	0.08	41.40	-

Electrolysis of the Salt Bath after Extraction

For electrolysis, graphite rods (Φ=4mm, LORRAINE PARIS) were used as electrode materials. Iron wire(Φ=5mm)was used as the lead wire. The electrodes were polished and washed in diluted HNO_3 solution to remove the possible impurities, and held above the salt melt 2-4 cm during the heating process. After the salt mixture was melted and held for dissolution at a fixed time, electrolysis started under 2.8V voltage supplied by a DC power (hp Hewlett 6632A) The experiments lasted for about 10-16 hours. After electrolysis, the electrodes were cooled down under the protection of Ar gas. The products on the cathode were washed by ethanol for SEM/EDS and XRD analysis.

RESULTS AND DISCUSSION

Dissolution of Slag/Chromite

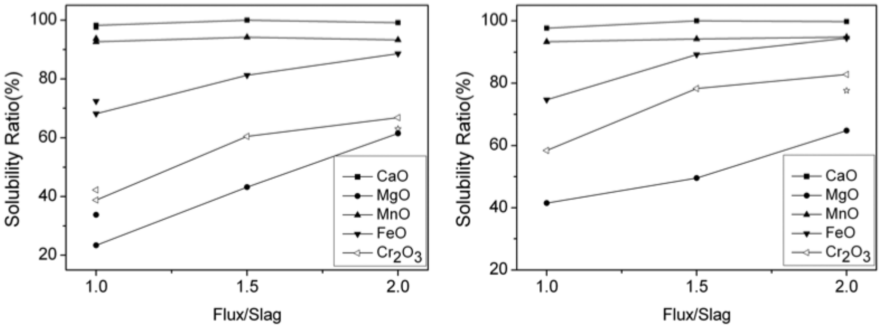
Figure 2 shows the standard Gibss energy change of metal oxides with the flux, it indicates that Al_2O_3 and SiO_2 cannot dissolve in the salt melt. Thus, these oxides can be separated as a residue after leaching the salt and slag phases after extraction in water at the end of the process. Two typical EAF slags, No. S1 and S2 with a high content of FeO and Cr_2O_3, respectively, as shown in Table 1, were employed in this investigation. Four factors, holding temperature, holding time, flux content (mole ratio to NaCl-KCl mixture) and flux/slag(weight ratio) were investigated.

Table 2: Solubility ratio of metal oxides in NaCl-KCl system

No.	**Solubility of metal oxides***					**Conditions**			
	CaO	**MgO**	**FeO**	**MnO**	**Cr_2O3**	**Temp.(°C)**	**Time(h)**	**Flux**	**Flux/Slag**
1	97,92%	7,23%	68,10%	93,84%	36,92%	850	6	20%	1.0:1
2	100%	31,88%	88,35%	98,18%	55,52%	850	8	25%	1.2:1
3	99,73%	35,59%	82,37%	94,68%	56,92%	850	10	30%	1.5:1
3I	98.81%	33.48%	78.36%	95.16%	55.79%	850	10	30%	1.5:1
4	100%	79,80%	83,83%	92,08%	58,37%	900	6	25%	1.5:1
4I	99.21%	70.36%	79.25%	91.88%	57.39%	900	6	25%	1.5:1
5	99,82%	17,39%	71,66%	90,76%	48,23%	900	8	30%	1.0:1
6	100%	31,86%	91,40%	97,26%	55,27%	900	10	20%	1.2:1
7	100%	46,89%	84,97%	91,24%	55,97%	950	6	30%	1.2:1
8	98,83%	80,88%	82,29%	89,28%	68,16%	950	8	20%	1.5:1
8I	99.25%	74.55%	78.86%	90.35%	66.20%	950	8	20%	1.5:1
9	90,61%	13,14%	83,36%	96,59%	48,24%	950	10	25%	1.0:1

$$* \ \frac{W\_MOx(slag) - W\_MOx(residue)}{W\_MOx(slag)} * 100\%$$

For slag No. S1, an orthogonal experimental design was employed. The chemical compositions of the residues after the dissolution are shown in Table 2. From this table, one can see that most of CaO, MnO and FeO can dissolve into the salt phase, while half or more Cr_2O_3 can be dissolved, and the dissolution is in the order of 'CaO>MnO>FeO>MnO/Cr_2O_3'. Some of the ICP-AES results (3I, 4I, 5I are results of the filtrate of the corresponding residue of 3, 4 and 5) are also listed in Table 2. They are in good agreement with ones from chemical analysis. Since very low content of MoO_x in slag, in view of the accuracy of the chemical analysis, it's difficult to determine the solubility ratio of MoOx precisely. But experiment No.4 showed that the *MoO* in the slag after extraction was 0.04wt%, with a solubility ratio of 73.42%. However, Mo is not detected in the ICP solution, probably due to the loss of $MoCl_x$ in the vapour phase during the salt extraction step. A variance analysis of the results shows that the importance of the factors follows the order, 'flux/slag ratio>flux content>holding time>holding temperature'. The weight ratio of flux/slag ratio was observed to have a strong impact on the dissolution of the slag. Since excessive flux adds to the cost and as the flux can not be recovered after the extraction process, it is necessary to find out the optimal process parameters, especially with respect to the flux content in the salt melt. In this case, detailed investigations were carried out on slag No.S2 with the help of ICP-AES element analysis.



(a)

(b)

Figure 3: The solubility ratio of slag No. S2 against the weight ratio of flux/slag. (a) At temperature 950°C, holding time of 8h and flux content of 20%. The star(☆) stands for the value of solubility ratio of pure Cr_2O_3 at the same condition. Other symbols stand for the value at temperature 950°C, holding time of 8h and flux content of 25%. (b) At temperature 950°C, holding time of 8h and flux content of 30%. The star(☆) stands for the value of solubility ratio of pure Cr_2O_3 at the same condition.

Figures 3-6 show the variation of the solubility ratio of various metal oxides corresponding to slag No. S2 due to different process parameters. One can see that the solubility ratio of CaO shows a very high value around 100%, while MnO is about 90%. These oxides do not represent a significant variation with the change of experimental conditions. These results are consistent with those obtained for slag No. S1. In Figure 3, three flux ratios used, viz. 1:1, 1.5:1 and 2:1 represent insufficient, sufficient and excessive amount of flux respectively. One can see the solubilities of the oxides FeO, Cr_2O_3 and MgO show significant change. Under the same condition, the increase of flux content can improve the solubility ratio of FeO, Cr_2O_3 and MgO. But the excessive amount of flux/slag ratio, viz. 2.0, does not contribute to a significant increase in the solubility ratio of Cr_2O_3. Consequently, in the experiments that followed, the flux/slag of 1.5 was employed. Similar results for dissolution of chromium value from chromite ore can also be observed in Figure 7. The solubility ratios of FeO and Cr_2O_3 increase with the increase of flux content (mole ratio to the salt mixtures), holding temperature and holding time. But these increases are less significant, as shown in Figures 3-6. Based on the results, the optimized process parameters were chosen as (a) temperature of 950°C, (b) flux/slag at 1.5 or 2, (c) holding time of 8 h and (d) flux content of 30%.

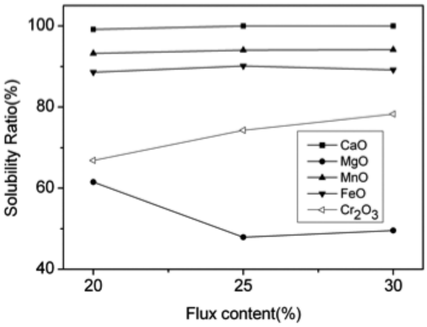


Figure 4: The solubility ratio of slag No. S2 against the flux content at temperature 950°C, holding time of 8h and flux/slag at 1.5

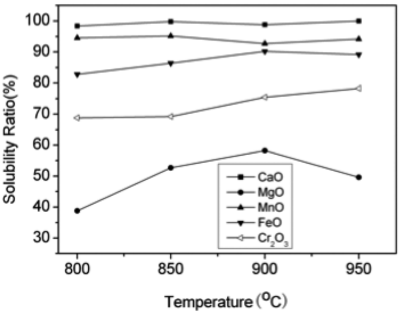


Figure 5: The solubility ratio of slag No. S2 against the holding temperature at holding time of 8h and flux content of 30% and flux/slag at 1.5

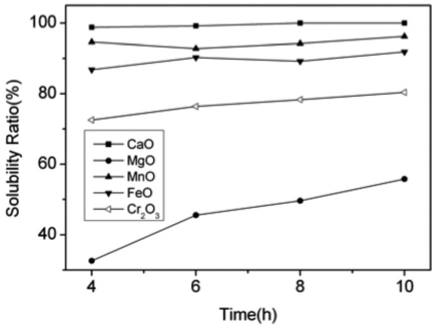


Figure 6: The solubility ratio of No. S2 slag against the holding time at temperature 950°C, flux content of 30% and flux/slag at 1.5

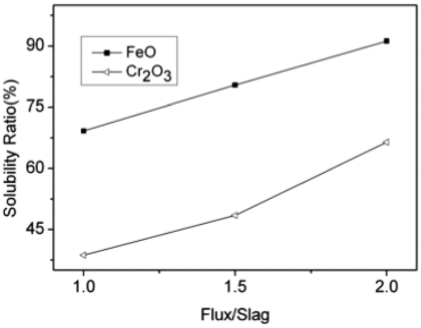


Figure 7: The solubility ratio of No. C1 chromite against the flux/slag ratio at temperature 950°C, flux content of 30% and holding time of 8h

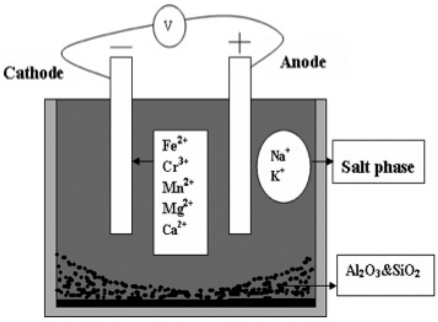


Figure 8: The schematic diagram of the selective electrolysis method

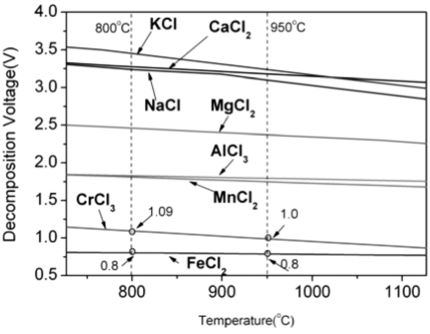


Figure 9: The theoretical decomposition voltage of different metal chlorides

Electrolytic Recovery

The dissolution test proves that the metal oxides in EAF slag/chromite can be extracted into the salt phase. The corresponding ionic states for the cations are likely to be Fe^{2+}, Cr^{3+}, Mn^{2+}, Mg^{2+} and Ca^{2+} together with Na^{+}, K^{+}. The higher valency states of Cr and Fe may be neglected as the extraction has been carried out under low oxygen partial pressures in high purity argon. The schematic diagram of the selective electrolysis method is shown in Figure 8. Under different cell potentials, the various metals or alloy can be deposited on the cathode surface. The theoretical decomposition voltage plotted in Figure 9 can give us a trend as $FeCl_2>CrCl_3>MnCl_2>AlCl_3>MgCl_2>NaCl>CaCl_2>KCl$. It shows that Fe and Cr can deposit first. Taking account of the higher cell voltage requirement and the lower content of Mn^{2+} and Mg^{2+} in salt phase, under a cell voltage of 2.8V, ferrochromium alloy is likely to be the main product. It should be noted that, the electrodeposition of metals can be affected by a number of factors even in pure molten salt systems, as for example,over voltage, current density, current efficiency, electro-bath conductivity, the nature and surface of the cathode material and distance between electrodes, etc. In the present work, several electrolysis tests on EAF slag/chromite were carried out with promising results.

A typical photo of the cathode products after electrolysis of slag is shown in Figure 10. The deposit consists of FeCr-rich alloy with a low amount of oxygen and salt mixtures or some undissolved slag. After removing the adhered product and washing the cathode with ethanol, a typical SEM image of the deposited product could be obtained which is shown in Figure 11. A dendrite-like structure of the crystal deposit could be observed in this figure. Further EDS analysis of the dendritic crystal presented in Figure 11 shows that it consists of Fe, Cr along with low content of oxygen(below 10%) and a small amount of Ca, Na, K and Cl. It should be noted that the oxygen content in this EDS analysis is not accurate. The present experiments show clearly that ferrochrome can be recovered from the slag by the combined extraction-electrolysis process. XRD results of the adhered substances on the cathode confirm the formation of Fe-Cr, as shown in Figure 12. The cathode products are mainly composed of Fe-Cr, inclusions of NaCl and KCl from the electrolyte apart minor levels of other impurities.

Figure 10: A typical photo of the cathode product after electrolysis

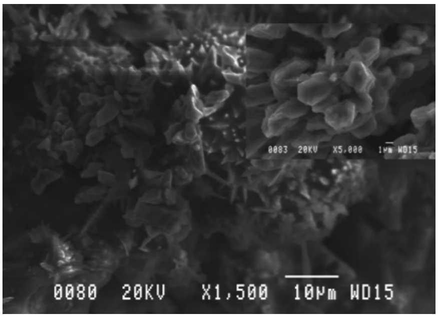


Figure 11: Typical SEM image of cathode product of No. S1 slag after 10h electrolysis at 950°C, holding time of 8h, flux content of 25% and flux/slag=1.5. Voltage 2.8V, current density:~150mA-250mA/cm^2

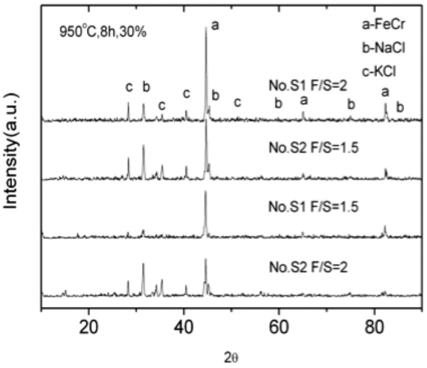


Figure 12: XRD patterns of the cathode products of slag electrolysis

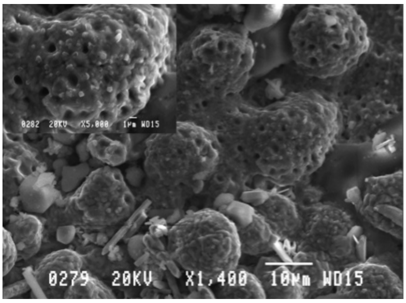


Figure 13: Typical SEM image of cathode product of No. C1 chromite after 10h electrolysis at 950°C, holding time of 8h, flux content of 30% and flux/chromite=2. Voltage 2.8V, current density:~150 mA-250 mA/cm^2

Similar electrolysis experiments were also tested on chromite ore. Typical SEM images of the cathode product from these experiments are shown in Figure 13. The EDS analysis of the image shows that it consists of 38%wt Fe, 56%wt Cr and small amounts of Na, K, Ca and Cl. Other crystals shown in this figure consist mainly of Na, K and Cl.

The present results show that this new process is quite promising. One important problem in the current series of experiments is that the cathode product is easily contaminated by the undissolved slag. Since it is very difficult to collect all the products after electrodepostion due to the bad adherence of the cathode products, the current efficiency and recovery ratio of metal values could not be determined. As the cathode area in the present series of experiments is small, a high current density at the beginning of electrolysis can easily bring about dendritic crystallization, which can make the metal more difficult deposit on the cathode surface. Thus, the future work on this process will be concentrated on the improvements on the electrodepostion process.

Some of the problems associated with the electrolytic process can be solved by up-scaling the process. In the case of the laboratory experiments, the crucible size is very small, which would lead to the undissolved slag coming into contact easily with the cathode. This will not only decrease the conductivity of the salt bath, but also contaminate the cathode surface. Consequently, it would be more difficult to get a good cathode deposit with good adherence. But, in a plant trial with a very large volume of equipment, it is expected that the undissolved slag could easily fall down and the pure salt phase would be on the top. Selective electrodepostion of the various metals and alloy extracted by the salt melt can be carried out without contamination. An effective separation of the slag residue and salt melt is also enabled. In a plant trial, careful design of cathode and anode can avoid the situation of imposing a very high current density during the electrodepostion. This would be of great help in obtaining a dense and high quality deposited layer. The introduction of cathode bag might also be also helpful in collecting the cathode products.

CONCLUSIONS

A novel salt extraction process was proposed in the present work. By this process, it is possible to recover various metal values from slags from alloy steel production, low-grade ores and even spent refractory linings. The process consists of a salt extraction step and an electrolytic deposition step. In the present work, the process was applied to the recovery of Cr from EAF slags and chromite ore. The dissolution properties of these raw materials were examined in detail. It was found that most of CaO, MnO in the EAF slag would be transferred to the slag phase. Cr_2O_3 and FeO also have a high solubility ratio and can be effectively transferred to the salt phase. Based on the present results, the optimized process parameters were (a) temperature of 950ºC, (b) flux/slag at 1.5 or 2, (c) holding time of 8h and (d) flux content of 30%.

Based on this, several electrolysis tests were performed with the salt extracts of chromium containing EAF slags as well as chromite ore carried out under optimized conditions. The SEM/EDS and XRD results shows the cathode deposit are Fe-Cr-rich product. A better performance of this process is expected when the process is up-scaled due to the larger volume of electrolytic cell. A combination of the two steps would lead to a continuous process for the recovery of chromium and other metal values from slags, low grade ores as well as spent refractories.

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