UTILIZATION OF SPENT REFRACTORIES AS SLAG FORMERS IN STEELMAKING

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Abstract

Large quantities of refractory wastes are generated in the steel industry. Due to contamination by slag and metal as well as compositional changes during use, it is possible to recycle only a portion of the spent refractories into new refractory products. The similarity in chemical and mineralogical composition of slag formers and refractories used in steelmaking, provides for the possibility of using spent refractories as slag formers. In this article the potential for using MgO- and Al_2O_3-containing waste brick as slag conditioners is investigated. Spent magnesia and dolomite refractories can be used to saturate slags with MgO to thereby reduce the wear of the lining in BOFs as well as in EAFs. Trials were carried out at SSAB Tunnplåt in Luleå where crushed magnesia-carbon brick was charged to the converters as slag additives, thereby reducing the added amount of dolomitic lime. No deviation in slag or steel analysis from normal practice could be observed. Wastes with high concentration of alumina can potentially be used as a fluxing agent in ladle slags. At Fundia Bygg in Mo i Rana the possibility of substituting the conventional fluxing agent with spent brick was examined. The results are promising and continued studies will be carried out in industrial as well as laboratory scale.

1 INTRODUCTION

During the production of metals, considerable amounts of wastes and by-products are generated. It is increasingly realised that landfilling of these materials is not acceptable and that wastes have to be managed in an environmentally sound manner. Companies also have begun to recognise the potential economical benefits that recycling of by-products may have. Spent refractories are, however, recycled only to a limited extent. MEFOS has initiated a co-operation project among metal and refractory producers in Nordkalotten, the arctic area of the Scandinavian countries, aiming to expand the recycling of spent refractories. The area is home to several steelmakers as well as ferroalloy and non-ferrous industries, all of which utilize high-temperature processes requiring vessels lined with refractory materials. Consequently, the generation of refractory wastes is substantial and through co-operation and exchange of ideas, the potential is good to find solutions for the management of these materials.

2 RECYCLING POTENTIALS FOR SPENT REFRACTORIES

Many aspects must be taken into consideration when aiming to find use for spent refractories. Factors such as a company's ability to remove, store, sort, beneficiate and transport material all influence the choice of recycling route for the spent material. Refractory recycling programs are thus to a large degree company specific, but experience have shown that without a strong driving force, imposed by internal or external pressure, recycling efforts are difficult to implicate in practice.

2.1 Sorting and Handling

A basic requirement for obtaining efficient recycling of spent refractories is well-developed systems for stripping and separation of the waste. Different types of wastes must be kept separated already at the source, or the efforts to sort the wastes will be immense. Separation is complicated by the use of vessels with mixed linings such as steelmaking ladles, see Figure 1. Commonly, spent ladle linings make up the largest refractory waste stream in a steel plant, thus their recycling could significantly minimise the waste volume. Figure 5 shows the breakout of material from a ladle. A properly designed system with procedures for breakout that are strictly followed, provides for that different refractory types can be kept apart. In most cases a perfect separation cannot be obtained and unless limited handsorting is practiced, the chosen applications must tolerate some mixing of foreign material.

2.2 Possible application areas

Spent refractories can be utilised in a number of applications, including:

- New refractories
- Slag conditioner
- Cement component
- Concrete aggregate
- Road aggregate
- Glass raw material
- Soil stabilization and conditioner

Characterisation by identification of impurities and quantification of their levels are important in the aim find a suitable use. Due to impurities such as slag, metal and other foreign materials introduced through insufficient sorting, only a portion of the waste bricks can be recycled into new bricks. Recycled refractories are usually more suitable for the manufacture of unshaped refractories for casting, gunning, and ramming applications. For many waste streams alternative applications may have to be considered.

3 USE OF SPENT REFRACTORIES AS SLAG FORMERS

The similarities in chemical and mineralogical composition of slag formers and refractories used in steelmaking, provide good possibilities for using spent refractories as slag additives in metallurgical processes. Compared to utilising the waste for producing new refractories the slag forming application is relatively insensitive to slag and metal contamination. A number of factors will have to be considered when evaluating the possibility of using a source of spent refractory as a slag former. It is important that the temperature is high enough and that good mixing is provided in the application intended to assure that the crushed refractory waste is dissolved.

3.1 MgO-containing waste refractories

Saturating FeO-rich slags with MgO is important for reducing refractory wear. If the MgO concentration of the slag is too low, the slag will be corrosive and dissolve MgO from the lining. The precipitation of MgO in the form of the solid solution magnesio-wustite also aids slag foaming. The amount that has to be added in order to saturate the slag depends on various factors such as slag basicity. In Figure 3 the MgO content at dual saturation of MgO and Ca_2SiO_4 in the CaO-SiO_2-FeO-MgO system is shown [4]. The figure defines the minimum amount of MgO required in the slag to be compatible with basic refractories. It can be seen that a slag with low basicity has high solubility of MgO. To reduce unnecessary wear of the bottom of the furnace it is thus important that MgO is added initially in a heat. A source of magnesia can be spent doloma and magnesia refractories which can be added as slag formers to converters as well as to EAF-furnaces.

3.1.1 Addition to BOF

An example of where waste refractories is utilized for its content of MgO is at Dofasco in Hamilton, Canada [1]. Here crushed MgO-C brick from the BOF and from the ladles in the fraction 5/8 inch to 4 inches (16 to 100 mm) is used as a slag conditioner and slag splashing additives to aid in extending the life of the lining. The brick is added to the slag remaining in the BOF at the end of a heat. Although the additions are known to extend the life of the lining it is not clear by which mechanism.

MEFOS conducted trials at SSAB Tunnplåt in Luleå with recycling spent MgO-C bricks from the BOF as a slag additive [2]. The brick was to be used in the BOFs as substitute for part of the burnt dolomite that is normally used as a slag additive. The brick was crushed and screened and material in the fraction 5 to 25 mm was put into big-bags in 300 kg lots. Figure 4 shows the crushed material. One big-bag was charged to each converter heat together with the initial scrap charge. The amount of dolomite added was reduced at a rate corresponding to its MgO content. Thus, in these trials 600 kg less dolomite was added to each heat and to make up for the lost CaO, extra lime was added. Spent brick was added to a total of 34 heats in both converters and process data and slag samples from these were compared to 35 reference heats conducted before and after the trials. Figure 5 and Figure 6 show the CaO- and the MgO-content of the slag in charges with and without spent brick addition. As the Figures show, no difference in slag analysis can be detected between heats with and without brick addition. No tendency could either be seen on other parameters such as steel yield and steel analyses.

3.1.2 Addition to EAF

The use of spent MgO-containing refractories as slag conditioner in electric arc furnaces is practised at several steel plants throughout the world. The effects on slag chemistry and changes on refractory wear due to the additions are however not well documented. Normally crushed MgO-C and dolomite-C brick are added together with dolomite and lime to the furnace. A concern with adding spent refractories is that they are hard-burned, which may reduce their dissolution rate. However, a laboratory study on burnt dolomite with various porosities showed no effect of apparent porosity on the dissolution rate [3].

In the United States the Albany Research Center and the Steel Manufacturers Association are conducting a joint research program with the main goals to improve the life of slag line refractories in the EAF and to recycle the spent refractory materials [1]. Refractory recycling and reuse is concentrated on in-house applications since it is believed that this has the greatest chance for implementation. Part of the research program studies the optimal MgO content of the slag to obtain good slag foaming. Pretorius [4] has studied this relation and states that the ideal content is near MgO saturation which gives a creamy slag with good bubble retention.

Spent dolomite bricks from the ladles are charged as slagformers to the EAF at Fundia Bygg in Mo i Rana, Norway. The dolomite bricks are torn out according to procedures that minimizes the mixing with the alumina safety lining. Norsk Ildfast Resirk AS (NIR), a refractory recycling company with facilities adjacent to the steel plant, prepares the brick through crushing, magnetic separation and screening. The product amounts to approximately 1000 tons per year and is then brought back to Fundia Bygg and put in silos for charging to the EAF.

3.2 Al_2O_3-containing waste refractories

Due to the ability to enhance de-oxidation and the high sulfide capacity, calcium aluminate-based slags are commonly used during the ladle refining step of steelmaking. The addition of alumina to calcium rich slags lowers the melting point and results in a fluid slag. The source of alumina is normally synthetic slag conditioners or bauxite, but these materials can often be substituted with spent alumina-containing refractories.

The distribution of sulfur between slag and metal is given by the equilibrium:

$$[S] + (O^{2-}) = (S^{2-}) + ½O_2(g); \qquad k_S = (\%S)\frac{[a_O]}{[a_S]} \qquad [1]$$

For a given oxygen activity the sulfur partitioning coefficient between slag and metal is calculated by:

$$L_s = (\%S)_{slag}/[\%S]_{metal} \qquad [2]$$

Iso-sulfur partition curves can then be established in oxide phase diagrams with a given oxygen activity fixed by an oxide/deoxidizer equilibrium [5]. Figure 7 shows the calculated sulfur partition coefficient in the system Al_2O_3-CaO-SiO_2 with 5% MgO and with the oxygen activity fixed by the equilibrium [Si]/SiO_2.

3.2.1 Trials at Fundia Bygg, Mo i Rana

The possibility of using waste brick as a ladle slag flux has been investigated at Fundia Bygg in Mo i Rana, Norway. Two test campaigns were conducted where the conventional slag conditioner, alumet, was exchanged with waste brick of two types. Table 1 compares the analyses of the waste brick and alumet.

The first type of spent refractory that was tested was alumina brick from safety linings. About 4 tons of brick was crushed and screened by NIR to obtain material in the fraction 0 to 8 mm. In order to minimize dusting the crushed brick was mixed a dust binder and the resulting material was put into bins and transferred to the ladle refining station at Fundia Bygg.

The results from the trials show that waste alumina brick works very well as a fluxing agent, but that the average desulphurization in these heats was somewhat lower than the average in heats using the normal practice with alumet. This may be expected since the alumina brick contains 26% SiO_2 and extra lime would have been necessary for its neutralization.

For the second test campaign 30 tons of spent spinel brick from SSAB Tunnplåt in Luleå was sent to Mo i Rana and NIR for crushing and screening and for subsequent use at the ladle furnace of Fundia Bygg. As with the alumina brick, the material was crushed to 0-8 mm and dust binder was added. As Figure 8 reveals, the spinel has a high melting point which was a concern prior to the trials since it was not certain whether the material would melt fast enough. However, the spinel brick appeared to dissolve rapidly into the ladle slag and worked well as a fluxing agent. The spinel has a higher Al_2O_3-content than alumet and the consumption of flux was also lower in the heats where spinel was used. The desulfurization was somewhat lower than the average in heats using alumet as a fluxing agent, but the removal of sulfur was sufficient.

In Figure 9 the desulfurization in heats using spent brick as a fluxing agents are compared to reference heats using the normal practice with alumet. The Figure clearly shows the dependence of sulfur removal on the sulfur content of the steel from the EAF. It is indicated by Figure 9 that the sulfur removal in heats using alumet is slightly higher than when spinel or alumina brick is used. In all heats, however, the sulfur removal was sufficient for the type of steel that is produced.

The main motivation to substitute alumet with spent brick as a fluxing agent is the potential to save money. Alumet and other alumina containing synthetic slag additive are fairly expensive and cheaper sources of alumina units to be used in the ladle slag is therefore desired. The average cost for slag additives, i.e. lime and fluxing agents, has been calculated for the three different practices using alumet, spinel and alumina brick. In Figure 10 the relative price compared to the alumet practice is shown. The figure shows that the cost of using spent brick as a fluxing agent is only about 50% of that of alumet, and thus substantial cost savings can be achieved.

The amount of furnace slag that is tapped into the ladle together with the steel varies between the heats resulting in that and therefore the total composition of the ladle slag will differ. Consequently the conditions for desulfurization will vary, thereby complicating the evaluation of the different fluxes on the basis on a limited number of heats. The actual effect of the addition of spent refractories to ladle slags is thus not completely clear. Laboratory tests will be carried out in which the slag forming caracteristics and desulfurization of the spent brick will be compared with alumet.

4 DISCUSSION AND CONCLUSIONS

Complete separation of different types of wastes as well as slag and metal impurities is often not possible. The incorporation of spent bricks in new refractories requires low and even levels of impurities, which in many cases are difficult to obtain. Large quantities of refractory wastes are therefore being landfilled every year. The application as slag former is normally not as sensitive to impurities, and spent MgO- and Al_2O_3-containing refractories can be used as slag formers in many steelmaking processes as alternatives to primary materials. This is also practiced at several steel plants.

Magnesia and dolomite brick is added to EAFs and BOFs to aid in saturating the slags with MgO to reduce the wear of the lining. The low porosity of spent brick may influence the rate of dissolution in the slag, but the effects on slag formation and lining wear is not well documented.

Expensive slag conditioners containing alumina are often utilized to flux ladle slags. It has been shown that spent brick in many cases can be used as substitutes for these materials. At Fundia Bygg in Mo i Rana trials have been carried out with using spent brick as fluxing agents in the ladle slag. Although the practice with using spent brick has not been optimized, sufficient sulfur removal could be obtained. Calculations based on the trials showed that substantial cost savings can be realized by exchanging alumet with spent alumina-containing refractories.

The examples shown here, indicates that there is substantial potential in using spent refractories as slag formers in steelmaking processes. However, it is also clear that further investigations have to be completed in order to elucidate the effects on slag formation, refractory wear and refining capacity. The optimal recycling solution is specific for each plant and depends on types and amounts of refractory products that are used as well on the available equipment for processing of the waste. Other factors such as landfilling costs and transportation distances will also influence the economics of the recycling. Increased recycling of spent refractories can only be accomplished through involvement of generators as well as the potential users of the wastes.

5 REFERENCES

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6 FIGURES

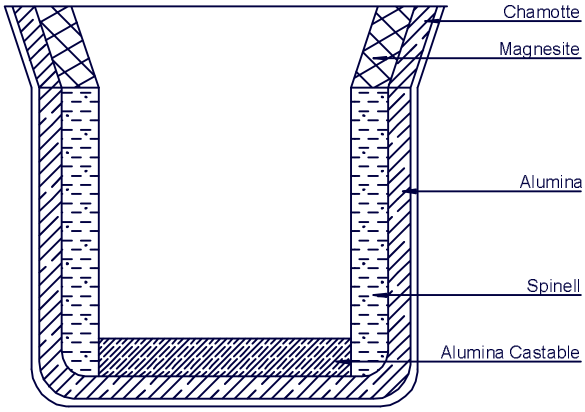

Figure 1 – Example of Mixed Refractory Materials in a Ladle Lining

Figure 2 – Breakout of Brick from a Steelmaking Ladle

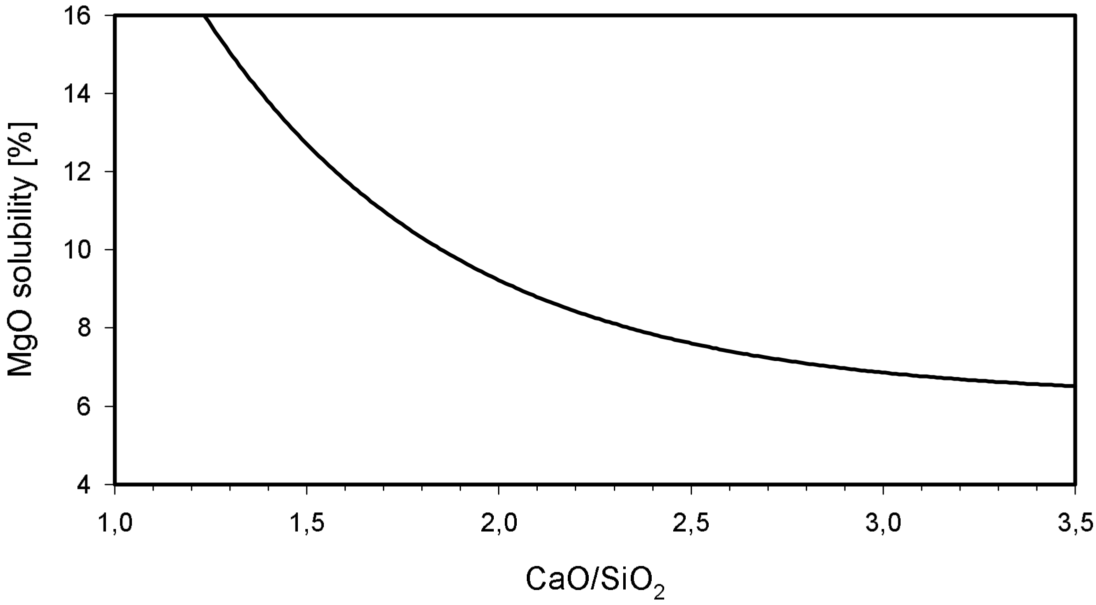

Figure 3 – Solubility of MgO in Slags that are Saturated with Respect to CaO and MgO [4]

Figure 4 – Crushed MgO-C Brick from the Converter

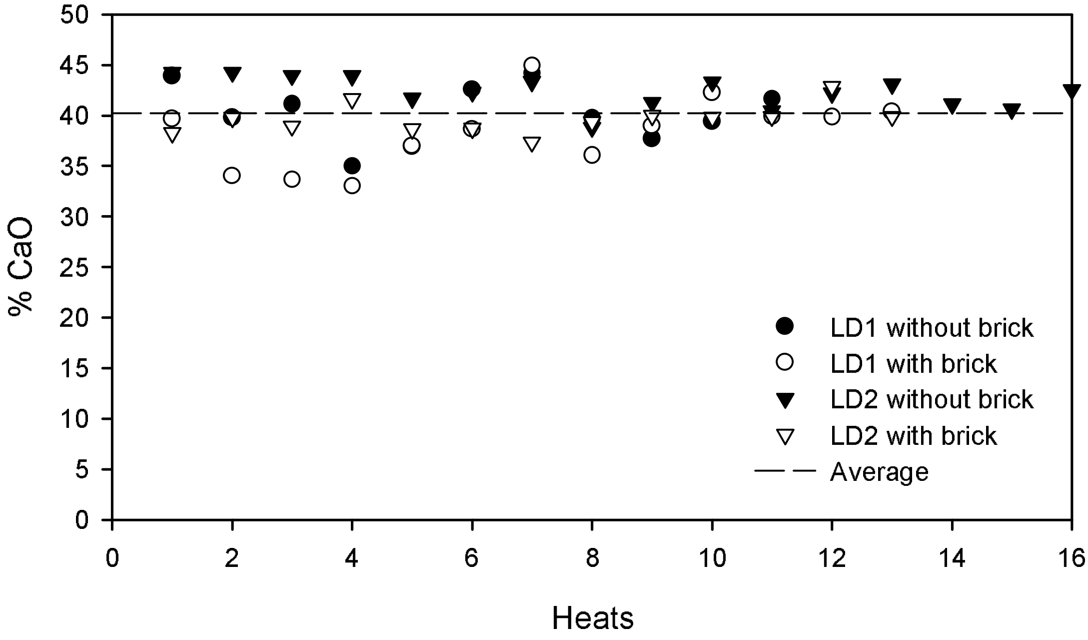

Figure 5 – CaO Content of the Slag in Heats with and without Spent Brick Additions

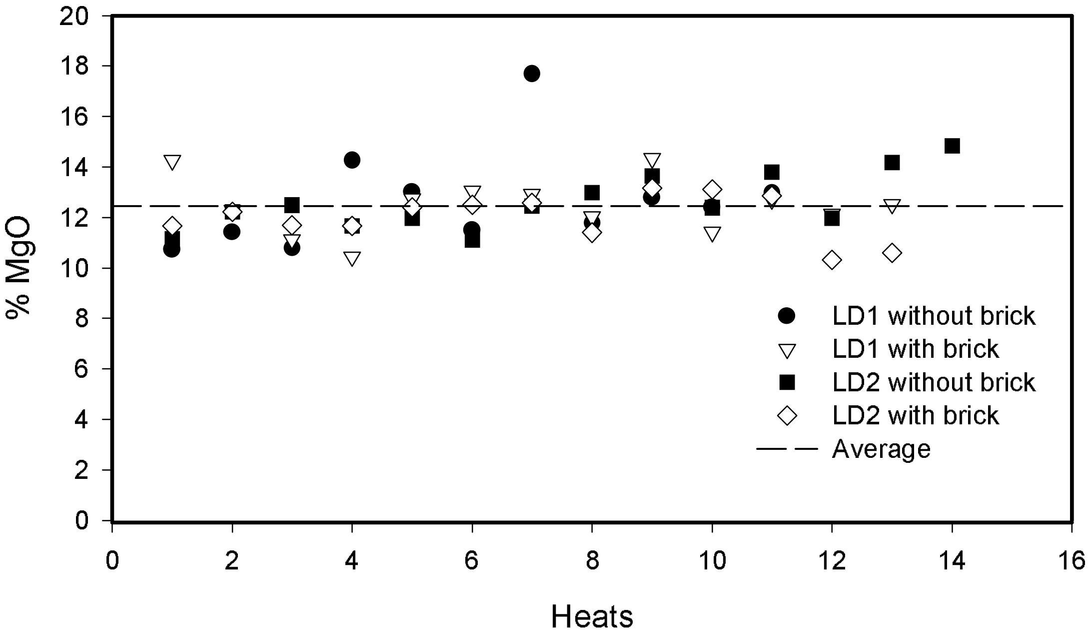

Figure 6 – MgO-Content of the Slag in Heats with and without Spent Brick Additions

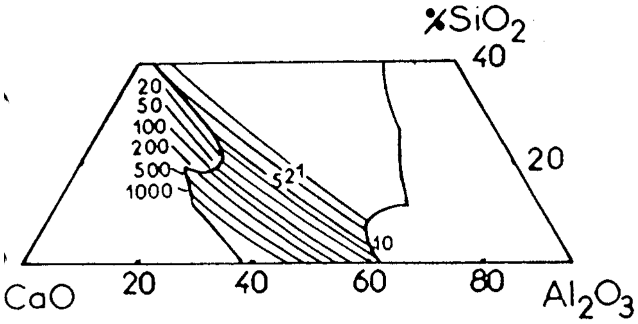

Figure 7 – Calculated Sulfur Partition Coefficient Between Slag and Metal at 1600°C in the System Al_2O_3-CaO-SiO_2 with 5% MgO and with the Oxygen Activity Fixed by the Equilibrium [Si]/SiO_2 with $a_{[Si]}$=0.4

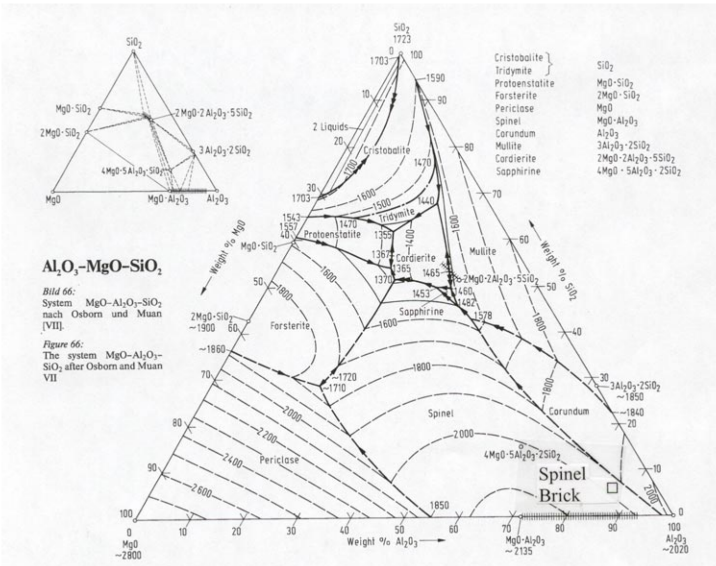

Figure 8 – The System Al_2O_3-MgO-SiO_2 System with the Composition of the Spinel Brick Indicated [5]

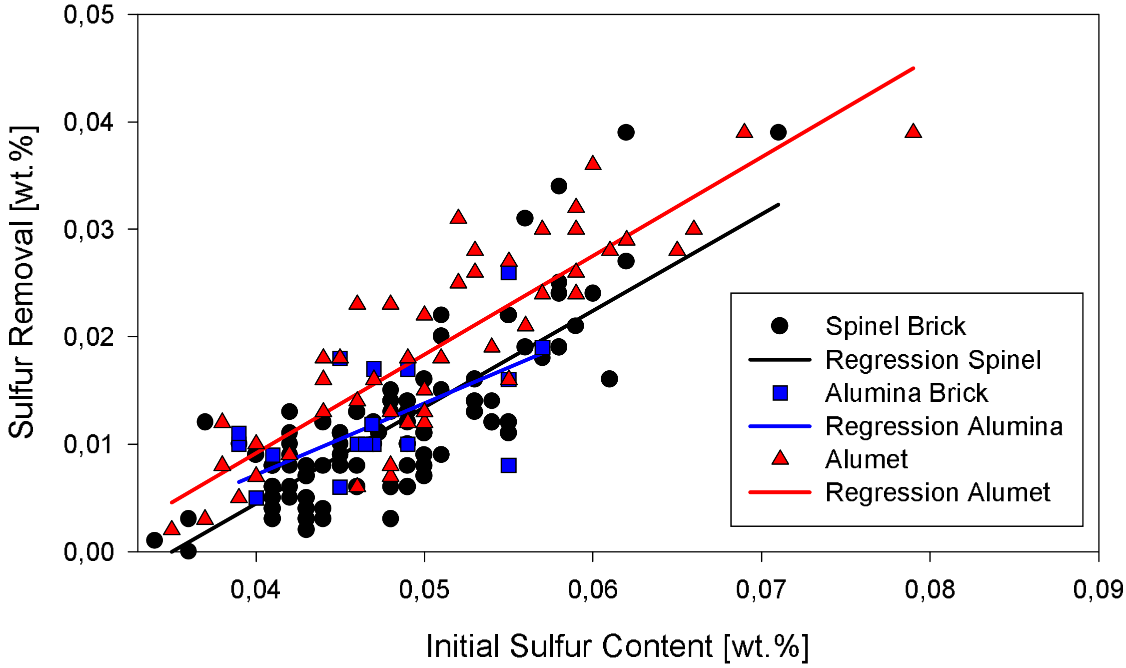

Figure 9 – Comparison of Desulfurization Using Spent Brick and Alumet as Fluxing Agents

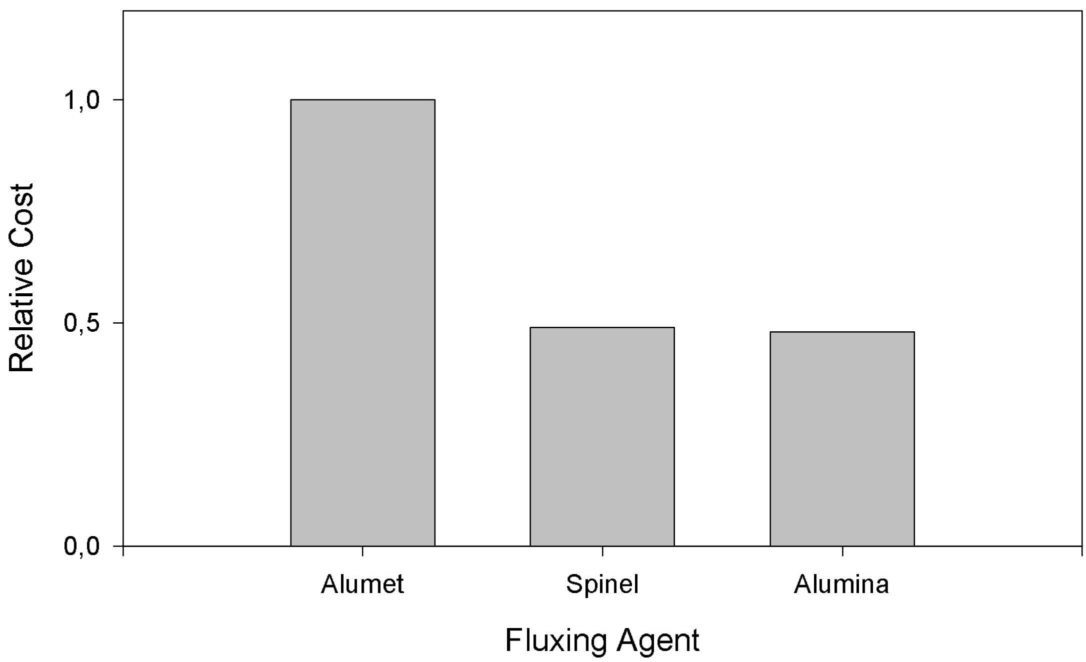

Figure 10 – Relative Cost of Fluxing Ladle Slags for the Various Fluxing Agents

7 TABLES

Table 1 – Analyses of Fluxing Agents in Weight Percent

	Al_2O_3	CaO	MgO	SiO_2
Alumet	60	25	9	
Alumina brick	62	3	3	26
Spinel brick	86		7.5	3.5