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# RECOVERY OF GERMANIUM FROM LEAD BLAST FURNACE SLAG

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## ABSTRACT

Laboratory scale test work was conducted to recover Germanium and other potentially valuable metals such as zinc, molybdenum and arsenic from accumulated lead blast furnace slags containing up to 100kg/ton zinc and 400g/ton germanium. The slag was smelted under reducing conditions in an electric arc furnace to produce a liquid alloy containing primarily iron (65-71%) and valuable metals (Ge: 0.2 – 1.1%, Mo: 0.8 – 4.5%, As: 2.6 – 9.3%). Zinc was volatilized and recovered separately as a condensate. The laboratory test work involved re-smelting of the above alloy phase at 1300°C and 1400°C with soda ash for various periods of time in order to transfer the valuable metals from the molten alloy into the molten soda slag phase. The latter phase was leached first in an alkaline medium and the concentrations of the elements were determined in the leach solution. The solid residue from the first leaching operation was again leached using sulphuric acid to increase the overall recovery of valuable metals. It was established that the total recovery of both germanium and arsenic to the leach solutions would be over 95% by this dual leaching procedure.

## 1. INTRODUCTION

A subsidiary of a major South African company operated a number of mines and non-ferrous smelters in southern Africa. Over the years, substantial amounts of metallurgical slags primarily from lead blast furnace have accumulated containing some 100kg/t zinc and 400g/t germanium as the main pay metals in addition to lead, arsenic, molybdenum and others. Numerous projects have been undertaken<sup>1-5</sup> to recover some of these metals in a saleable form with limited success. This presentation discusses the non-confidential parts of the studies undertaken which involved the smelting of the slag under reducing conditions in an electric arc furnace to volatilize and then recover zinc as a condensate, while 60-70% of the germanium, and most of the arsenic, molybdenum and copper are collected in an alloy phase that consist mainly of iron. Analyses of two typical alloy samples are shown in Table 1.

Table 1. Composition of two alloy samples obtained from smelting of lead blast furnace slag

Element	Concentration(kg/t)	
	Sample 1	Sample 2
Iron	657	706
Carbon	18	17
Zinc	1.8	0.4
Copper	158	87
Arsenic	26	93
Molybdenum	8.5	45
Germanium	1.94	11.11
Gallium	0.735	0.259

In this experiment study, germanium as the most valuable element in the alloy was targeted and its transfer from metal to a caustic slag phase was investigated followed by leaching to recover it.

## 2. EXPERIMENTAL PROCEDURE

The metallic alloy samples were received in powder form from the company. The designated alloy of 4 grams was carefully mixed with 4 grams of chemically pure  $\text{Na}_2\text{CO}_3$  in an agate mortar. The mixture was charged into an alumina crucible. This crucible was placed inside a one-size larger alumina crucible to prevent leakage and loss of samples. The crucible assembly was placed on a pedestal and raised slowly into constant temperature zone of a vertical molybdenum wound furnace. The furnace work tube was gas-tight, and the molybdenum wire heating elements were protected from oxidation by cracked ammonia gas supplied into the furnace shell from bottom of the shell and vented off from the top of the shell. The furnace temperature was controlled by thyristor fired euroterm controller activated by B-type thermocouples. The crucible was raised to the hot zone slowly over a period of 15 minutes. These smelting tests were conducted between ½ hours to 8 hours at 1300° and 1400°C.

It was earlier observed by preliminary tests that the alloy samples were fully molten above about 1270°C. At the end of the experiments, the crucible/pedestal assembly was rapidly withdrawn to the water-cooled bottom end of the furnace work tube so that the samples would solidify and cool rapidly. The crucibles containing the samples were kept in sealed desiccators. Slag-metal separation was achieved easily with no crucible failures. However, the removal of the samples from the crucibles could only be achieved by cutting and/or breaking the crucible itself. Any residual metal phase if

existed could easily be separated from the slag which was mostly stuck to the crucible. Thus; the samples together with the alumina crucible pieces were ground for two minutes by using siebtechnique and washed with water. The ground sample was subjected to so-called alkaline leach by using distilled water, the alkaline reaction of Na<sub>2</sub>O imparting the basic character on the ensuing solution, with pH values above 12 being measured in all the leach tests. The duration of these alkaline leach tests was 7 hours at 50°C. Again optimum time and temperature were determined in preliminary experiments. The leached samples were filtered and alkaline leach residues were washed through the filter paper, the amount of the solution being kept at a certain level for calculations.

A small amount of that alkaline solution was kept in a well-sealed sample bottle for chemical analysis. The alkaline leach residue was further leached with an acid solution using sulphuric acid in concentrations between 50 and 200g/l again for 7 hours at 50°C. The acidic leach residue (insoluble parts containing crucible debris, etc) was carefully filtered out with water and again the acidic solution was kept at a certain level for calculations. A small amount of the acidic solution was separated for chemical analysis. During both leaching operations the samples were continuously agitated using magnetic stirrers.

### **3. RESULTS AND DISCUSSION**

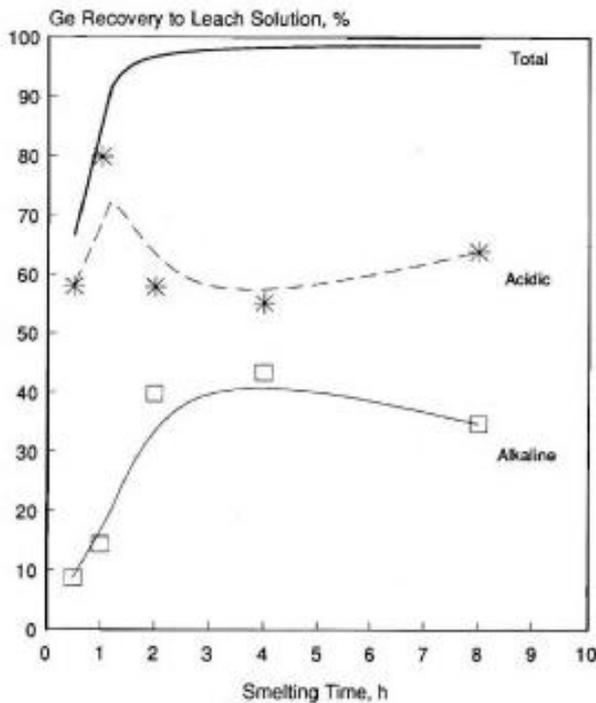
#### **3.1 Results**

The results are presented in graphical form through Figures 1 to 10 in form of recovery versus smelting time plots obtained from chemical analysis of the leach solutions. An accountability analysis was also performed for each species that was analyzed chemically. The accountabilities of iron varied between 92 and 102 percent depending on the experiments, that of germanium between 74 and 108 percent, that of Cu around 93 percent, that of arsenic between 91 and 119 percent and that of molybdenum between 59 and 91 percent. The accountabilities are by and large in an acceptable range except for iron which is rather good. The results for iron indicate that the experimental runs were satisfactory, but that there could be problems with analytical Procedure, mainly due to small sample sizes. Therefore the results have been calculated and interpreted by referring the amount of the various elements to a head value that was calculated for each element and each experiment separately from which recovery values were derived as a percentage.

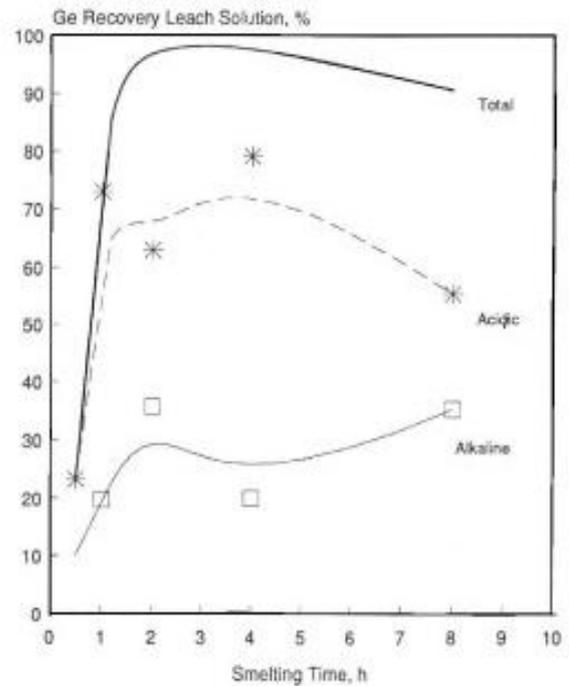
Figure 1 and 2; illustrate the germanium recovery in alkaline and acidic solutions as well as the total recovery as a function of smelting time at 1300°C and 1400°C respectively. Both figures indicate rapid increases in recovery within the first two hours and then a rather flat or even decreasing recovery profile. While the total recoveries reach +98%, the recovery in alkaline leach solution (the first leach) remain low around 40%. To reveal the effect of different leaching environments, Figures 3 and 4 are plotted

for germanium recovery (at both temperatures) illustrating the results of alkaline and acidic medium separately. From Figure 3, it is seen that for alkaline leaching the effect of temperature of smelting is rather small especially for shorter smelting periods. The situation is not far too different for acid leaching, however, as can be seen much higher germanium recoveries have been achieved.

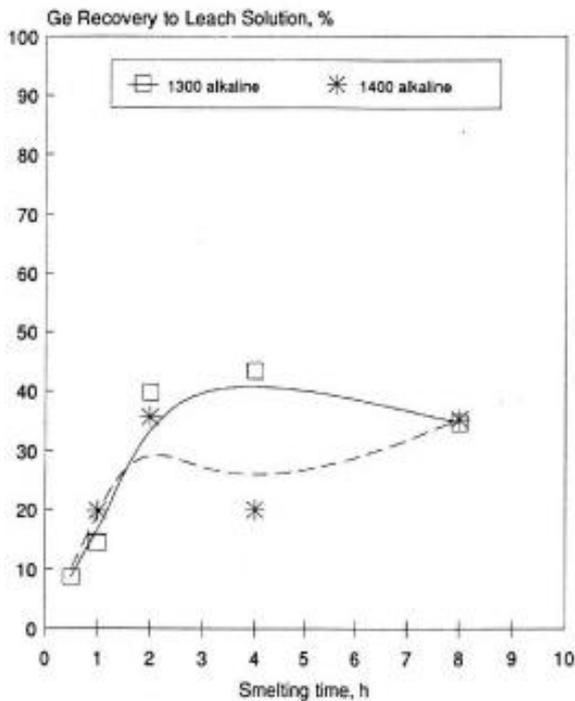
Figure 5 to 8 illustrate arsenic recoveries against smelting time at 1300°C and 1400°C as was done for germanium above for both alkaline and acidic leaching environments. At 1300°C an increase in smelting time increases the arsenic recovery linearly in alkaline medium. In acidic solutions the recovery increases sharply for the first 2 hours of smelting period and then decreases rapidly. Total recovery of close to 100% is achieved after about 3 hours. When the alloy is smelted at 1400°C, as shown in Figure 6 the total and thus individual recovery of arsenic in different leaching environments are lower than at 1300°C, again showing sharp increases for short periods of smelting. Figures 7 and 8 illustrate the arsenic recoveries in alkaline and acidic medium separately. In alkaline leaching of arsenic the behaviour of sample smelted at 1300°C is considerably different than that which was smelted at 1400°C. In alkaline solution the maximum recovery of arsenic reaches almost 80% (in 8 hours though) for samples smelted at 1300°C in contrast to about 60% recovery achieved by the sample smelted at 1400°C.



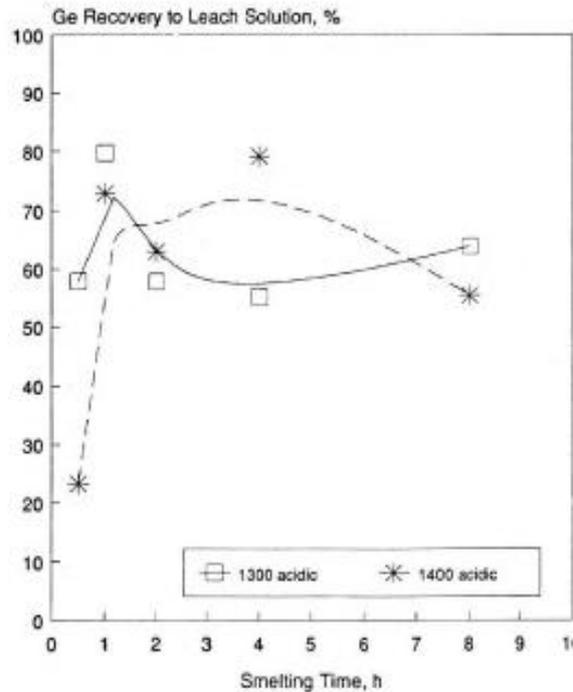
**Figure 1.** Germanium recoveries to different leach solutions after smelting at 1300°C.



**Figure 2.** Germanium recoveries to different leach solutions after smelting at 1400°C.



**Figure 3.** Germanium recoveries to alkaline leach solution after smelting at 1300 °C and 1400°C.

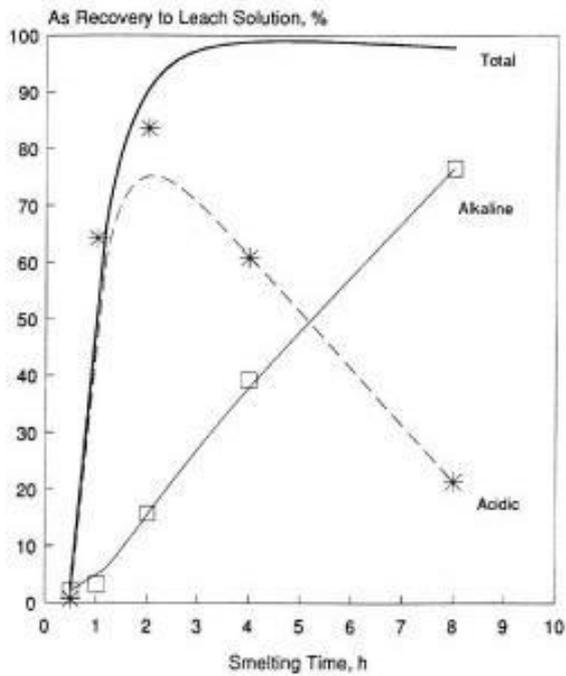


**Figure 4.** Germanium recoveries to acidic leach solution after smelting at 1300 °C and 1400°C.

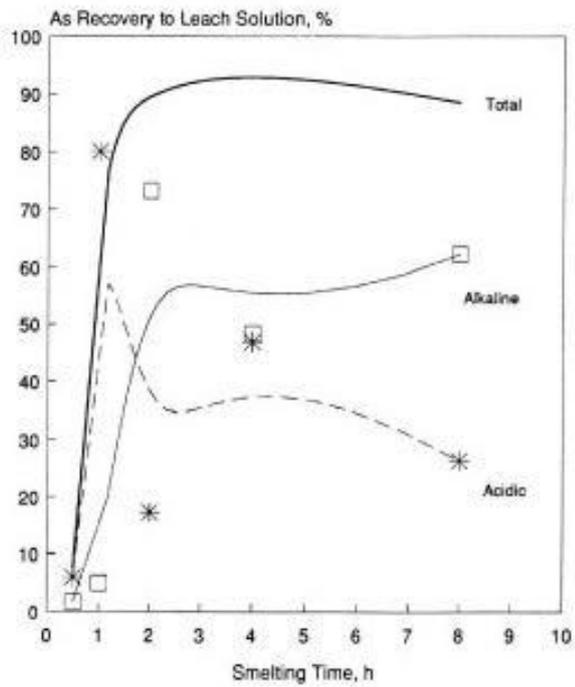
The lower recovery of arsenic at the higher temperature smelting can be attributed to the loss of arsenic to the gaseous phase in the form of arsenic oxide. At the higher temperature the vapour pressure of arsenic oxide is higher leading to higher losses and hence lower recoveries.

Figure 9 shows the effect of smelting time at both 1300°C and 1400°C on the molybdenum recoveries in alkaline solutions. The recoveries increase with smelting time and the effect is more pronounced at 1400°C after 2 hours, reaching a maximum of around 50%. The data for molybdenum in the acid leach was unreliable and hence no recoveries were calculated.

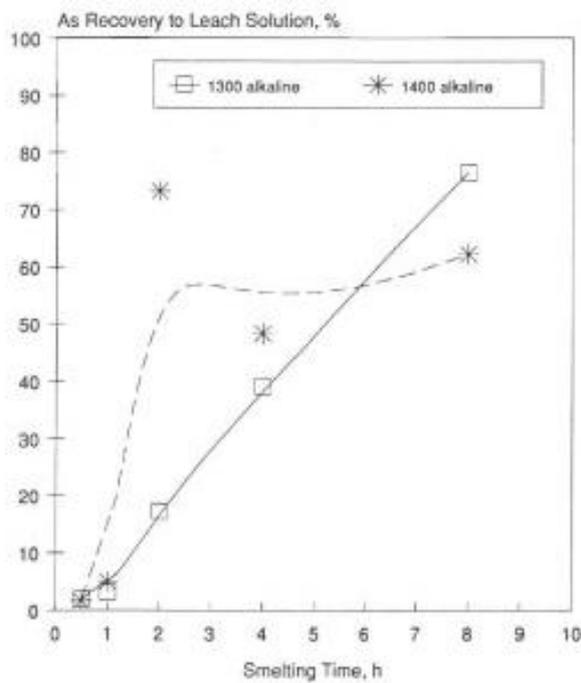
In Figure 10, the iron recoveries in acidic leach solutions for samples smelted at 1300°C and 1400°C are plotted against smelting time. In general, recoveries increase with increases in smelting time, although the difference between recoveries for samples smelted different temperatures is not very high.



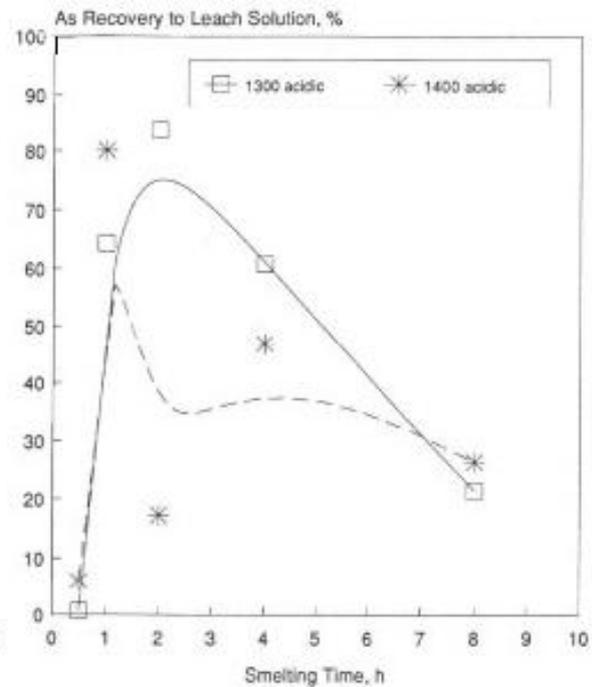
**Figure 5.** Arsenic recoveries to different leach solutions after smelting at 1300 °C.



**Figure 6.** Arsenic recoveries to different leach solutions after smelting at 1400 °C.



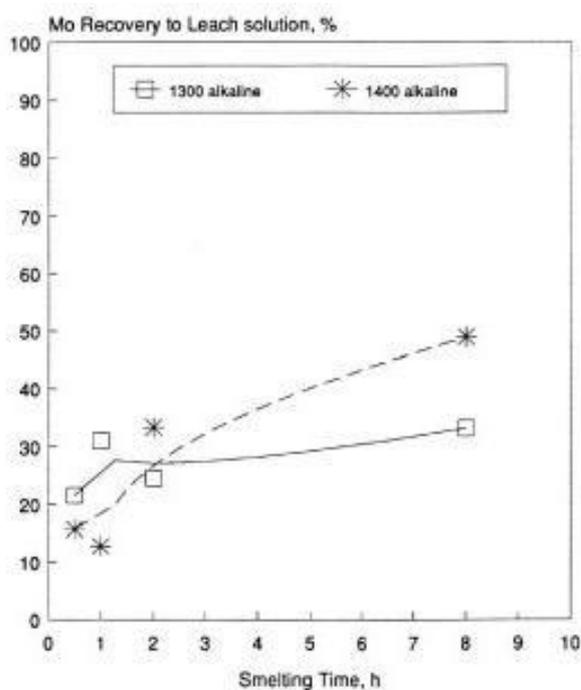
**Figure 7.** Arsenic recoveries to alkaline leach solution after smelting at 1300°C and 1400°C.



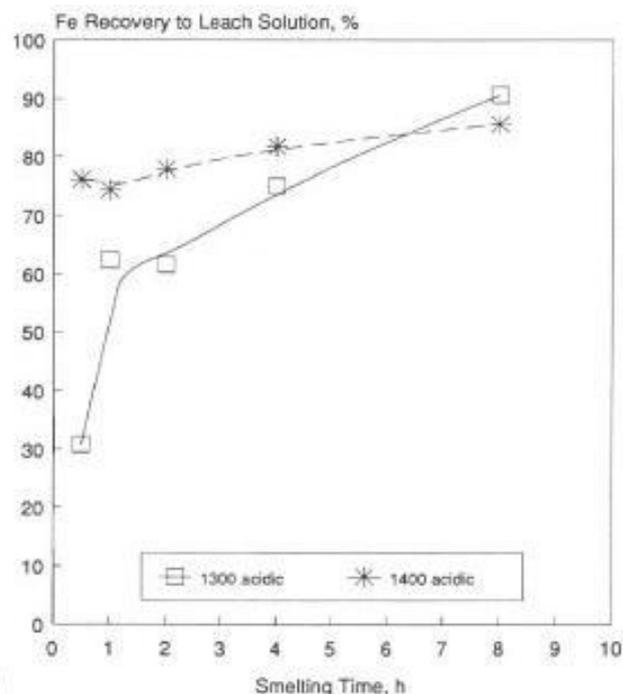
**Figure 8.** Arsenic recoveries to acidic leach solution after smelting at 1300°C and 1400°C.

### 3.2 Discussion

Although the smelting temperature affects the recoveries in alkaline solution leaching, its effect is not strong. Smelting period at both temperatures seems to influence the recoveries within the first few hours (around 2-3 hours) in most cases, and thereafter its effect is also limited. In the alkaline solutions recovery of germanium is rather low reaching a maximum of around 40%. Arsenic recovery is better at around 60%, where else molybdenum recovery reaches 50%. All these values are regarded as low, and it is apparent that the remaining germanium and arsenic are recovered in the subsequent acidic leaching. Iron is also recovered extensively in the acidic medium.



**Figure 9.** Molybdenum recoveries to alkaline leach solution after smelting at 1300°C and 1400°C.



**Figure 10.** Iron recoveries to acidic leach solution after smelting at 1300°C and 1400°C.

During the leach experiments, the alkaline leach residue had a brown colour which indicated the existence of  $\text{Fe}_2\text{O}_3$ . This was also confirmed by X-ray diffraction. The chemical analysis also showed that most of the iron was dissolved in the acidic solution. The iron oxide presumably forms during the highly oxidizing caustic smelting.  $\text{Fe}_2\text{O}_3$  might also form by the oxidation of iron during fine grinding but this second

source should be limited in amount. The presence of Fe<sub>2</sub>O<sub>3</sub> in the slag phase is believed to trap the oxidized germanium, rendering it more leachable under acidic conditions. Arsenic behaves similar to germanium, but it appears that its diffusion out of the iron oxide phase is faster yielding higher recoveries during alkaline leaching. Another interesting observation is the facts that during acid leaching recoveries of both germanium and arsenic reach a very high maximum, and then decrease as a function of smelting time. This presumably indicates that at longer smelting periods some of the oxidized arsenic and germanium is transferred back to the metal phase which is only soluble in acidic environment, but that the concentrations of these two elements are very low in the metal, so that their leaching is difficult. The back transfer of oxidized germanium and arsenic from the slag to the metal phase may occur due to the diminishing oxidation power of the soda ash for longer periods of smelting. With respect to molybdenum similar discussions can be provided despite the fact that the molybdenum data in acidic solution was unreliable. However, it was recovered at a maximum of about 50% in the alkaline solution. As expected, iron was recovered extensively in acidic medium.

#### **4. SUMMARY AND CONCLUSIONS**

Small-scale smelting tests of finely milled metal phase derived from lead blast furnace slags were carried out at 1300°C and 1400°C for various periods of time where the metal phase mixed 1:1 with soda ash.

Total germanium extraction was over 90% after about 4 hours. However, only up to 40% could be recovered to an alkaline leach solution; the remainder was apparently trapped in an iron oxide (primarily Fe<sub>2</sub>O<sub>3</sub>) phase and could only be solubilized by an acidic leach.

A similarly high extraction was established for arsenic, which also distributed between alkaline and acid leach solutions, but reporting preferentially to the former. It is believed that molybdenum behaves similarly, up to 50% reporting to alkaline leach solution.

One is therefore faced with the following dilemma. While oxidation is required to affect the transfer of metallic germanium hosted in the iron alloy to a caustic phase in which it must necessarily be present as a germanate (IV); the concurrent oxidation of iron creates an iron oxide phase that traps the better part of the valuable germanium in its lattice. Although conceivable, leaching by acid of the trapped germanium (arsenic, and molybdenum as well) is not easily incorporated into a flow sheet. Thus the effects of iron oxide trapping of germanium and the potential loss by volatilization of soda ash in industrial conditions are not conducive to make the molten metal/molten soda slag route for the extraction of valuable metals particularly attractive.

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