




RECOVERY OF GERMANIUM FROM LEAD BLAST FURNACE SLAG

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✓ Metallurgical slags primarily from lead blast furnace have been accumulated containing some 100kg/t zinc and 400g/t germanium as the main pay metals in addition to lead, arsenic, molybdenum and others

The Aim of This Study

- ✓ 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.
- ✓ 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.

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

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

EXPERIMENTAL PROCEDURE

- 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 is mixed 1:1 with soda ash (Na_2CO_3) in alumina crucibles.
- 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 a so-called alkaline leach by using distilled water, the alkaline reaction of Na_2O imparting the basic character on the ensuing solution, with pH values above 12 being measured in all the leach tests.
(7 hours at 50 C).
- The leached samples were filtered and alkaline leach residues were washed through the filter paper.
- 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.

RESULTS

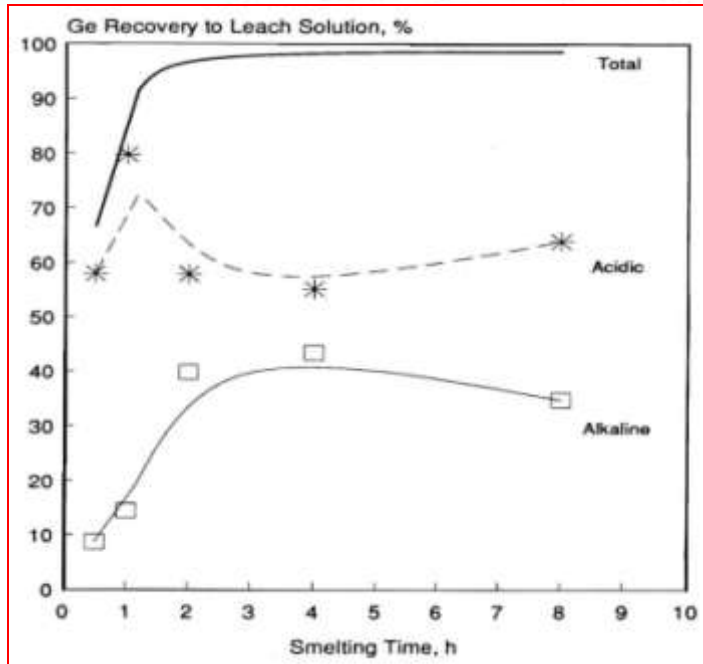


Figure 1. Germanium recoveries to different leach solutions after smelting at 1300 °C

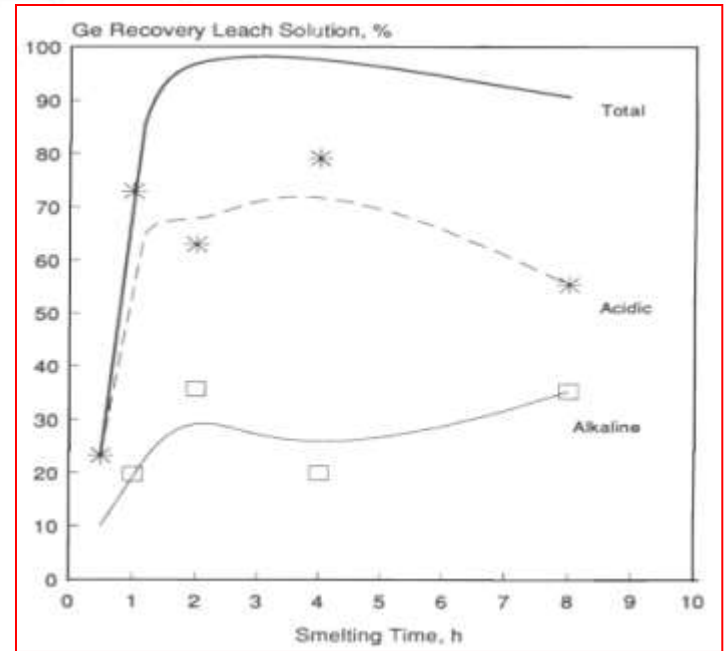


Figure 2. Germanium recoveries to different leach solutions after smelting at 1400 °C

- Rapid increases in recovery within the first two hours and then a rather flat or even decreasing recovery profile.
- The total recoveries reach +98%, the recovery in alkaline leach solution (the first leach) remain low around 40%.

RESULTS

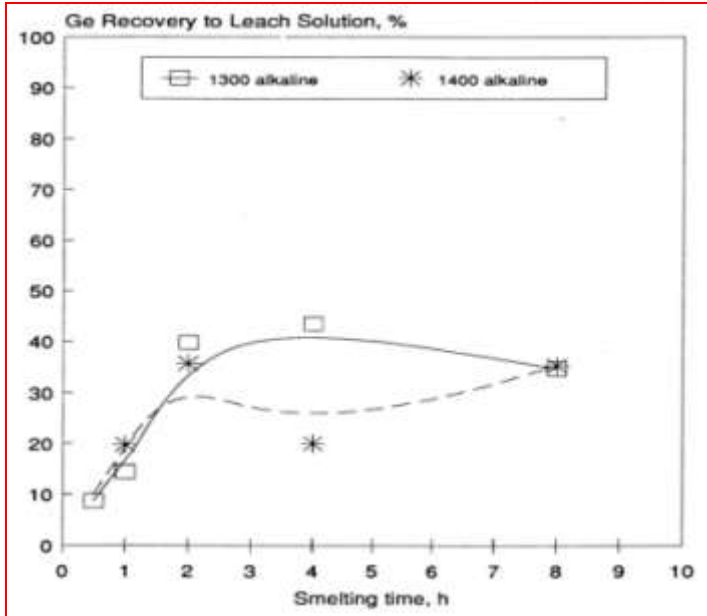


Figure 3. Germanium recoveries to alkaline leach solutions after smelting at 1300 °C and 1400 °C

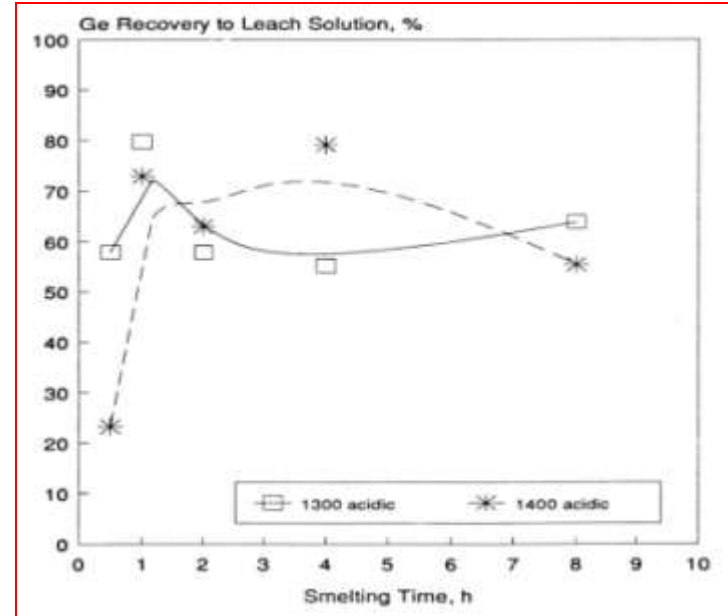


Figure 4. Germanium recoveries to acidic leach solutions after smelting at 1300 °C and 1400 °C

- In the 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.

RESULTS

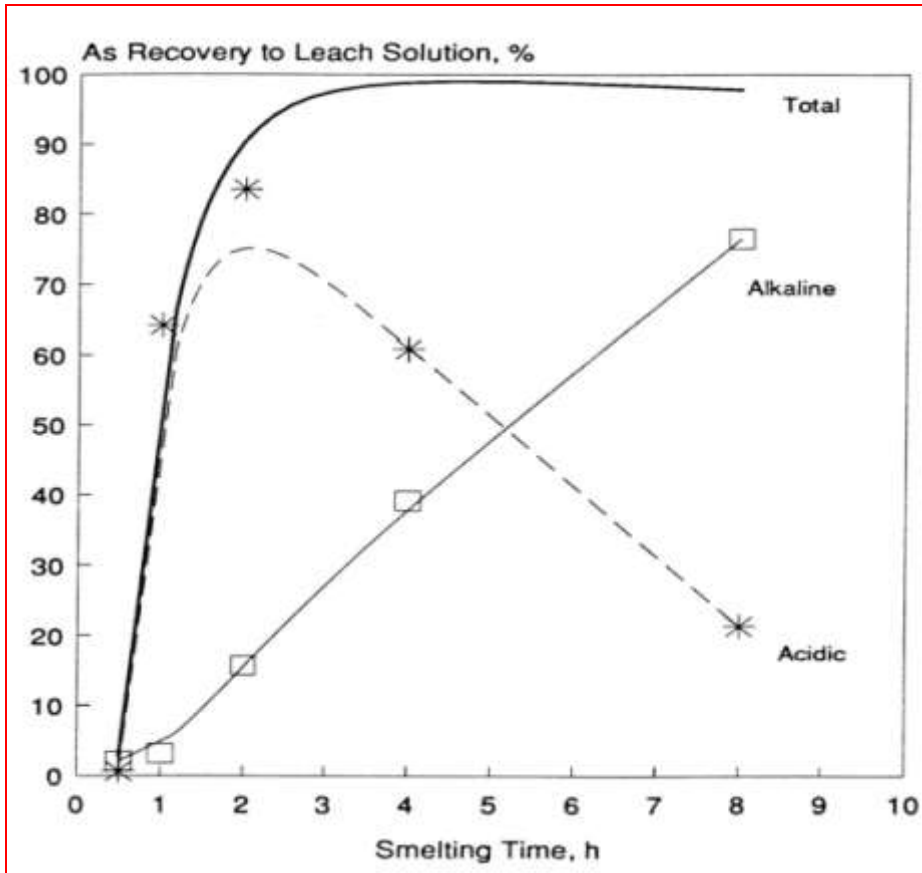
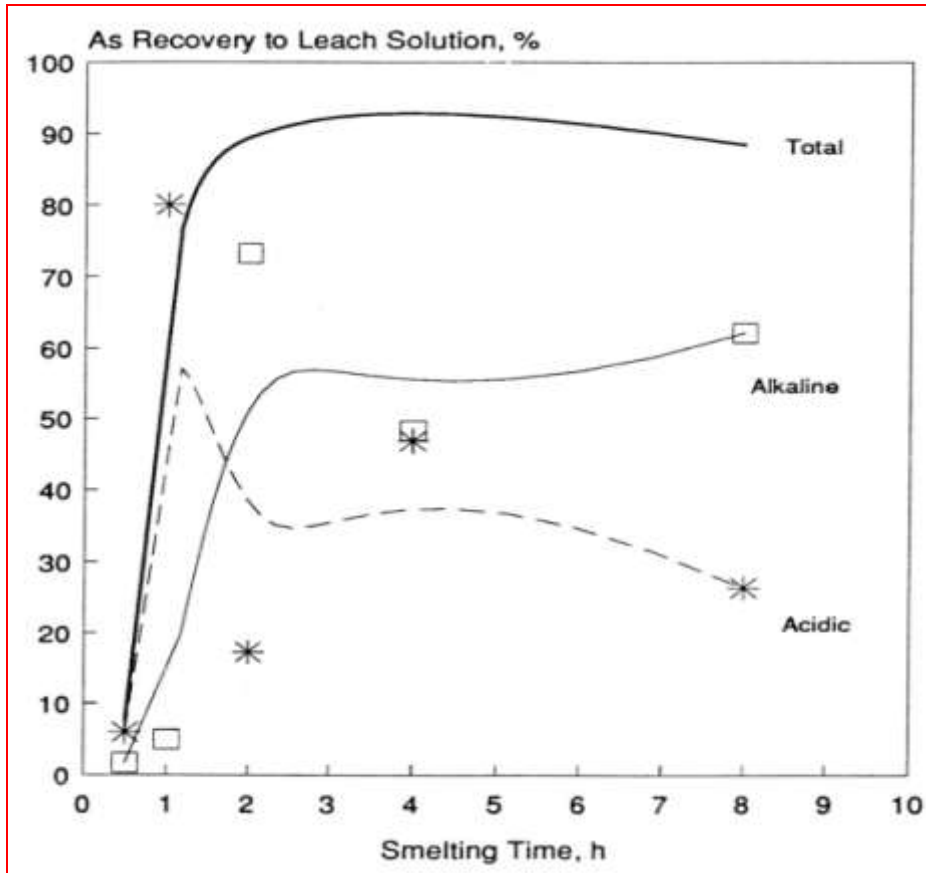


Figure 5. Arsenic recoveries to different leach solutions after smelting at 1300 °C

- 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.

RESULTS



•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

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

RESULTS

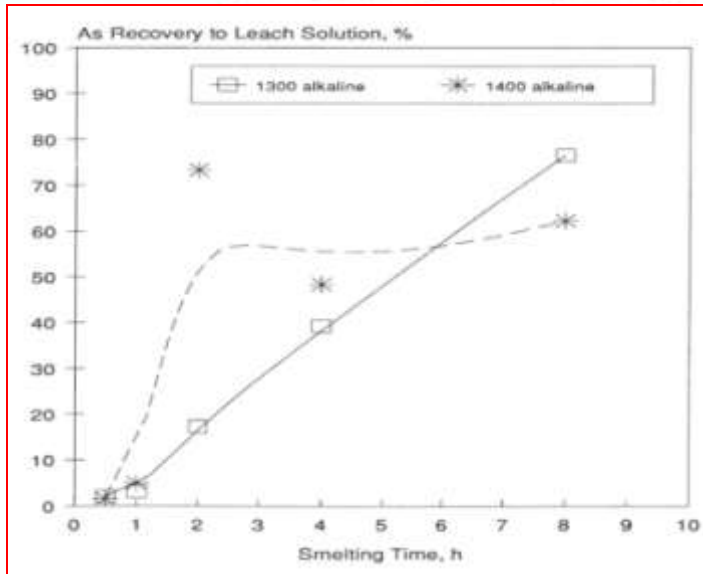


Figure 7. Arsenic recoveries to alkaline leach solutions after smelting at 1300°C and 1400°C

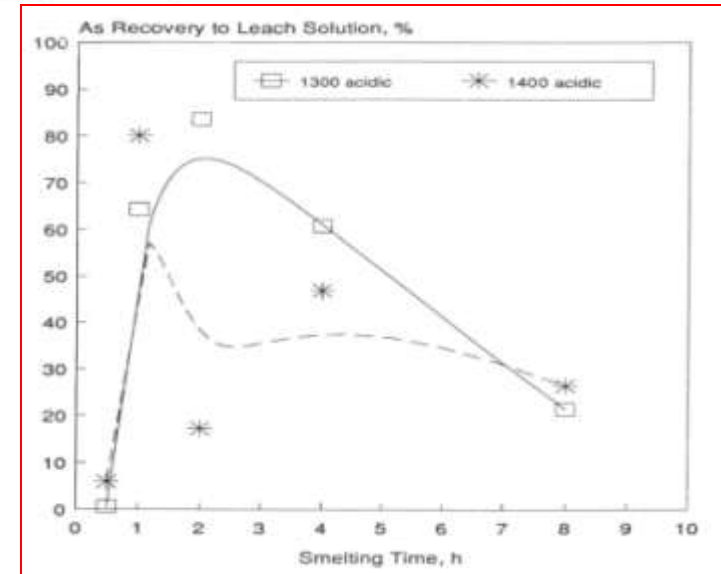


Figure 8. Arsenic recoveries to acidic leach solutions after smelting at 1300°C and 1400°C

- 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.
- 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.

RESULTS

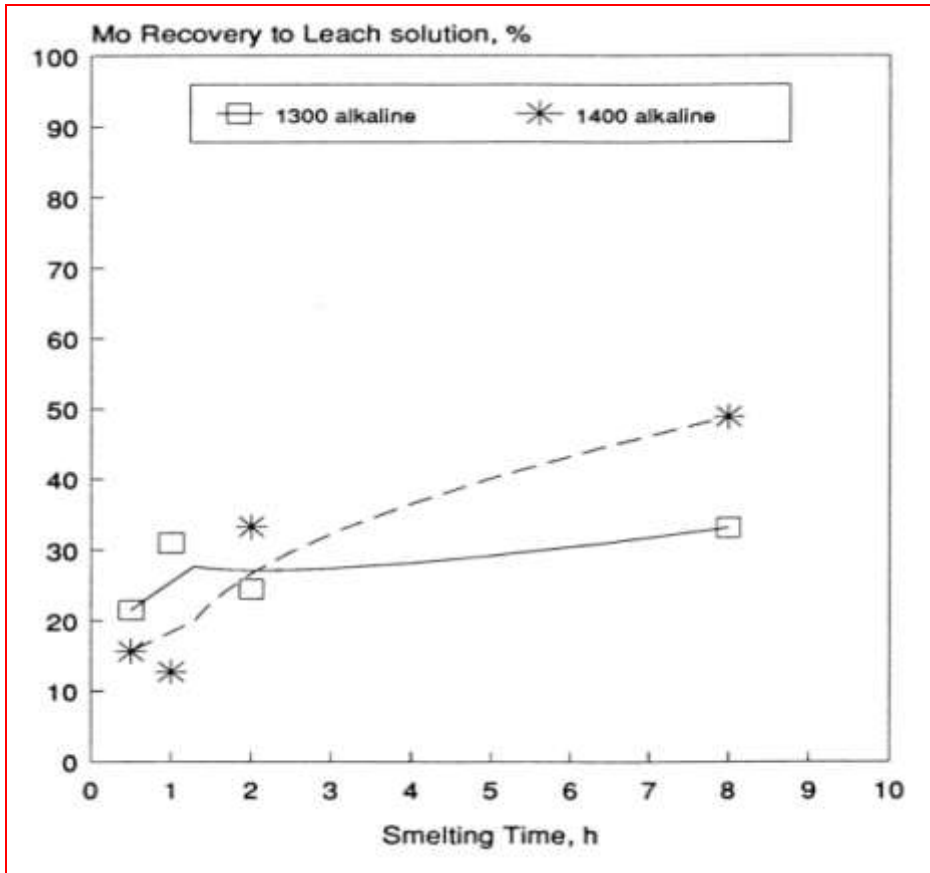
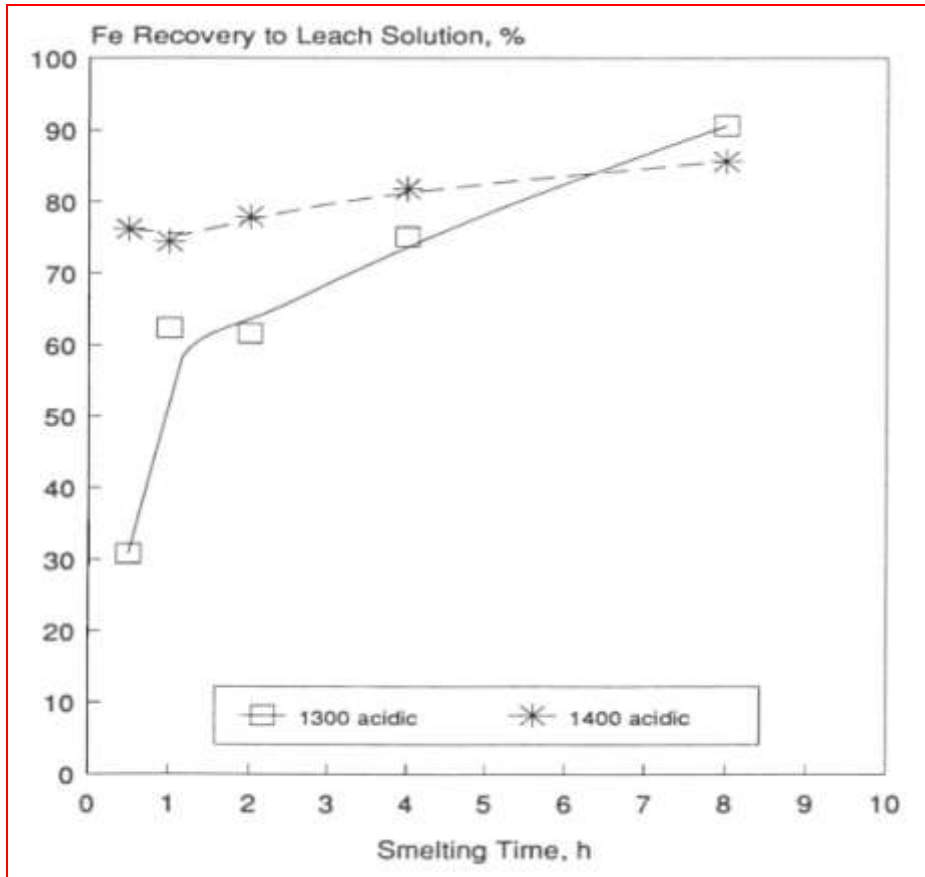


Figure 9. Molybdenum recoveries to alkaline leach solutions after smelting at 1300° C and 1400° C

- 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.

RESULTS



- Fe recoveries increase with increases in smelting time, although the difference between recoveries for samples smelted different temperatures is not very high.

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

DISCUSSION

- The smelting temperature affects the recoveries in alkaline solution leaching, its affect 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%.
- The remaining germanium and arsenic are recovered in the subsequent acidic leaching.
- Iron is recovered extensively in the acidic medium.

DISCUSSION

- Iron oxide presumably forms during the highly oxidizing caustic smelting. Fe_2O_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_2O_3 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.
- During acid leaching recoveries of both germanium and arsenic reach a very high maximum, then decrease as a function smelting time.
- 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 the concentrations of these two elements are very low in the metal, so their leaching is difficult.
- Molybdenum was recovered at a maximum of about 50% in the alkaline solution.

SUMMARY AND CONCLUSIONS

- Total germanium extraction was over 90% after about 4 hours.
- Germanium could be recovered only up to 40% to an alkaline leach solution; the remainder was apparently trapped in an iron oxide (primarily Fe_2O_3) phase and could only be solubilized by an acidic leach.
- Arsenic is mostly recovered in alkaline leach solution.
- Molybdenum behaves similarly to arsenic, up to 50% reporting to alkaline leach solution.
- 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.
- The effect 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