

A note on 'free-silica slags'

Over the last years, the term 'free-silica slags' has been employed frequently to characterise certain types of slag. These are smelting residues with inclusions of crystallised silica (quartz and/or cristobalite). They rarely exhibit flow textures. Their generally heterogeneous nature is indicative of furnace slags, i.e. slags which remained inside the reactor (furnace, hearth, crucible) at the end of the process. The silica inclusions in these slags vary in size from less than one millimetre to centimetres in diameter.

The explanations given for the genesis of 'free-silica slags' are not convincing (Kassianidou et al., 1995). The inclusions of quartz etc. are interpreted as relics of gangue or fluxes which have not reacted nor reached their melting point. How does this explain the often relatively large inclusions? Components of furnace charges (ores, fluxes) are crushed to small sizes prior to charging in order to increase their surface and thus help to promote reaction. Large fragments of gangue would most likely have been removed from the charge during beneficiation of the ore. The assumption that quartz had been added to the molten slag as 'stiffener' to increase its viscosity and thereby aid in the liquation of metals with low melting points, e.g. lead (Tylecote 1987, p. 306f.) refers to a routine used in lead smelting still practised in England and Scotland during the 19th century (Percy 1870, p. 238f.). Limestone was added to the slag in order to make it 'stiff' and prevent its flowing out of the hearth; only molten lead was tapped into the fore hearth. Quartz would have been the most unsuitable substance to add, because lead and silica react vigorously to form lead silicates with melting points from up to 700° C. If quartz had been employed for this purpose, the reaction would have resulted in severe losses of lead. During the smelting of copper ores, the 'stiffening' of slags with quartz, etc. would have made no sense either, because the metallurgists' intention is and was the optimal separation of metal and impurities, which is best achieved through formation of low viscosity tap slags.

In August 1997, the author witnessed smelting experiments at ValliPres near Aubusson in Central France, carried out by members of the Institute for Industrial Furnace Construction/Technical University Aix-la-Chapelle/Germany. The construction of the experimental furnace was based on archaeological evidence for Bronze Age copper smelting furnaces in the Austrian Alps, e.g. Mitterberg near Salzburg. Its height was about 50cm, the internal dimensions 45 x 30cm. Air was blown into the furnace front through two tuyeres (diameter c. 3cm) with a controlled flow rate of c. 40 to 60 l/min. The charge consisted of a pelletised synthetic ore (grain size 5mm) with the following composition: Cu₂O = 16%, Fe₂O₃ = 50%, SiO₂ = 18% and CaCO₃ = 16% (Woelk and Woelk 1997). The first experiments with CO/CO₂-ratios insufficient for complete reduction produced inhomogeneous, porous furnace slags with charcoal fragments and large white opaque SiO₂-inclusions, some of them more than a centimetre in size. They consist of quartz and cristobalite (Hauptmann 1997). The silica necessary for the formation of these inclusions was supplied by the ore, the furnace walls and the charcoal ashes. At the start of the experiment the charge was completely free from any visible quartz crystals or fragments. Thus, genesis and

growth of quartz-cristobalite inclusions was the result of reactions in the semi-molten state or of solid-state reaction. They can be explained as follows:

Under reaction conditions in the heating zone of the furnace which are not completely reducing, the Fe₂O₃-content of the ore is only converted to magnetite, Fe₃O₄, instead of to FeO. Reaction of magnetite with SiO₂ under the prevailing temperatures (ca. 1100°C) is extremely slow or totally absent. Only at temperatures above 1375° does SiO₂ react with magnetite to form Fe₂O₃ and fayalite slag respectively:



Silica is thus 'withdrawn' from reaction with iron oxide and can therefore form the polymorphic crystalline phases quartz and/or cristobalite (Tafel 1953, 257f). According to Budnikow (1853, 158f) other metal oxides, like hammer scale as well as other slag phases will promote crystallisation and transition of SiO₂-modifications and presumably their crystal growth as well.

In later smelting experiments, using the same furnace and the same type of synthetic ore, the conditions for reduction were optimised. This resulted in the formation of homogeneous fayalite tap slag, completely free from inclusions, and metallic copper (with only little adhering slag particles).

The occurrence of 'free-silica' slags' is apparently not restricted to base-metal smelting. It was also observed in the direct production of iron (bloomery process). In September 1997, Swedish magnetite ore was tentatively smelted in an experimental furnace built at Plas Tan y Bwch/Snowdonia National Park. The experiment did not produce a proper bloom, but only a lump of very heterogeneous furnace slag with scattered white inclusions, obviously of crystalline silica.

Based on these observations, it is postulated that 'free-silica slags' are indicative of magnetite formation (or conservation) within the furnace charge. Magnetite does not react readily with silica – at least not within the temperature range characteristic in early smelting practice. Silica molecules tend to form crystals which, under the influence of mineralising agents, can grow to considerable size. Further investigations, e.g. determination of magnetite contents in 'free-silica slags' are suggested and recommended to verify my hypothesis.

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