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## A Note on Metamorphism and Re-crystallization in Zinc Pellets during Roasting<sup>1</sup>)

By G. C. Amstutz (Rolla, Missouri, USA)<sup>2</sup>)

The genetic interpretation of rocks and ore deposits has gained considerably from comparisons with artificial processes. More than any other operation the smelting of ores produces conditions and products similar to those of magmatic and metamorphic cycles in the earth's crust.

The present paper is a preliminary note on such an example of artificial products. It reports about mineralogic changes in zinc pellets during roasting at low (950°C) and high temperatures (above 1000°C). The papers listed in the bibliography report about the physical chemistry of zinc roasting. No reference was found on the similarity with natural metamorphism and on the microscopic structure of pellets.

Raw zinc pellets naturally look the same as a polished section of a zinc concentrate (fig. 1). The bulk of angular particles is sphalerite or marmatite, with varying amounts of gangue, copper minerals, pyrite and galena. The binder, which is dispersed in the bakelite, consisted of ZnSO<sub>4</sub>. During roasting the following reactions take place and convert the sphalerite or marmatite concentrate into zinc oxide and Zn-Fe spinels — (franklinite):

$$(Zn, Fe)S + O_2 \rightarrow ZnO + ZnFe_2O_4 + SO_2^{\nearrow}$$
 (1a)

or: 
$$3ZnS + 2FeS = 2ZnO + ZnFe_2O_4 + 5SO_2^{7}$$
 (1b)

This reaction appears to take place during metamorphism (roasting) from the zinc concentrate to low temperature pellets (about

<sup>1)</sup> Published with permission of Cerro de Pasco Corporation.

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950°C, fig. 2). If heated up to 1000°C or higher, the following equation seems to be more appropriate:

$$(Zn, Fe)S + O_2 \rightarrow ZnO + Fe_3O_4 (+ZnFe_2O_4) + SO_2^{7}$$
 (2)

ZnFe<sub>2</sub>O<sub>4</sub>, franklinite, is put in parentheses because it forms in some cases only. The hard rims of agglomerated pellets showed numerous spinels with approximately ZnFe<sub>2</sub>O<sub>4</sub> on the outside (lower reflectivity) and approximately Fe<sub>3</sub>O<sub>4</sub> on the inside. The boundary between the white inside and the grey rims is fairly clear. We may thus assume that there exists a definite compositional difference, the two components corresponding to approximately that of magnetite and that of franklinite.

In many medium and high temperature pellets it was possible to observe a rim at the outside which contained only few, or no magnetite and franklinite crystals at all, but only zincite. Also, it is commonly observed that the waste heat boiler dust is richer in iron and lower in zinc than the pellets themselves. We must assume, therefore, that some of the iron from the outer shells of the pellets is migrating outwards during roasting. No explanation for this Fe-migration has been found so far. Some of the Fe may leave with S during roasting.

The migration of Fe towards the outside has been compared with that of Fe during oxidation of single minerals (artificial through kernel roasting or natural through alteration of ore deposits). The type of mineralogical change is, however, quite different. In an agglomeration like the pellets a migration takes place along grain boundaries and inside the interstitial spaces or fluids (if there are any fluids). In individual grains migrations must take place inside the crystal lattice. Many of these changes inside single grains may be due to dislocation.

Another remarkable feature of the high temperature pellets is their layered structure and the large grainsize. As seen in fig. 3, the zincite and the ferrites are arranged in layers. This is equivalent with metamorphic differentiation and re-crystallization (Sammelkristallisation) in metamorphic rocks. Banded iron deposits show similar arrangements between magnetite and quartz, and portions of New Jersey zinc deposits exhibit also similar structures. (Banding in Fe deposits is, however, generally interpreted as syngenetic.) The layering concerns also the grain size, because the outside is often fine grained whereas the inside is almost always coarse. This suggests that re-crystallization takes place from the inside out. Also ZnO grains are usually twice as big as the Fe<sub>3</sub>O<sub>4</sub> grains.

The composition as calculated from the assays is as follows:

average assay:	weight $\%$	atomic weight	atomic ratio
	70 % Zn	65	$101 \ \mathrm{Zn}$
	9.5% Fe	56	$16  \mathrm{Fe}$
	20 % O	16	125 O
	traces of S, Si, etc.		

average calculated mineralogic composition:

$$101 \text{Zn} + 101 \text{O} = 202 \text{ZnO} = 83.5\% \text{ZnO}$$
 (3)

$$17 \text{ Fe} + 23 \text{ O} = 40 \text{ Fe}_3 \text{ O}_4 = 16.5 \% \text{ FeO}$$
 (4)

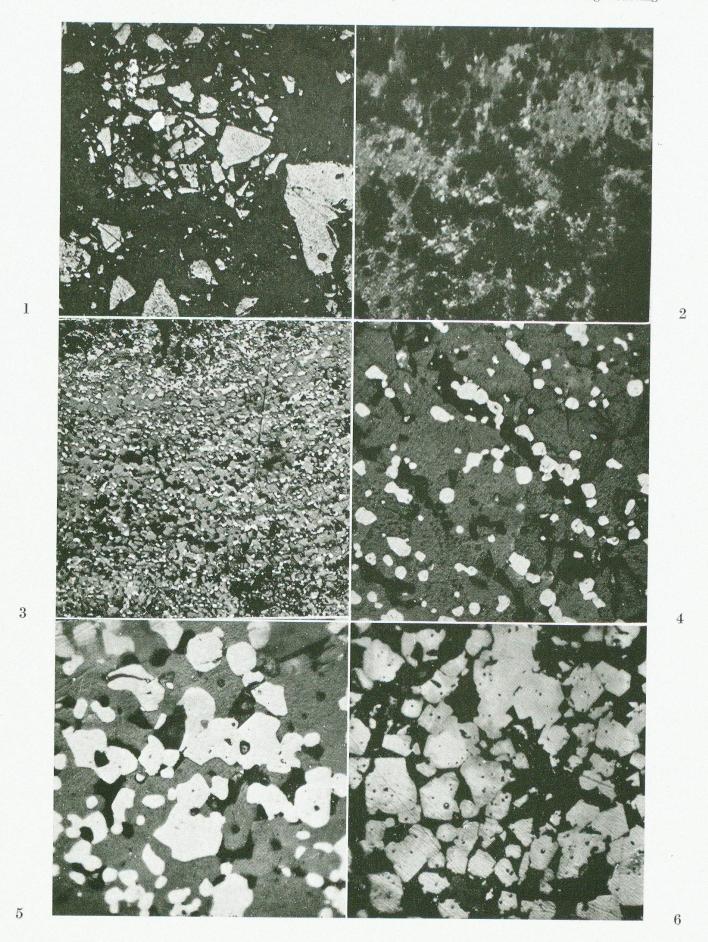
This corresponds well with the average composition as seen from the polished surfaces.

Some ZnO grains contain one-micron-size lamellæ of white mineral with the same reflectivity as that of Fe<sub>3</sub>O<sub>4</sub>. It is most probable that these lamellæ consist also of Fe<sub>3</sub>O<sub>4</sub>. The locking inside the ZnO grains may be inherited from the marmatite particles.

The average mineralogic composition of waste heat boiler dusts, which represent those parts of the pellets that are lost into the air during roasting, is as follows:

### Legend to the Microphotographs

- Fig. 1. Raw Oroya zinc pellet (pelletized Zinc concentrate). Composition: grey = sphalerite; white = pyrite and scarce particles of galena and chalcopyrite; black matrix is lucite. Scale 1:150.
- Fig. 2. Roasted zinc pellet; Oroya low temperature calcine ( $\pm 950^{\circ}$  C) ZnO=dark grey, ZnFe<sub>2</sub>O<sub>4</sub>=light grey, with reddish-brownish interior reflexes; Fe<sub>3</sub>O<sub>4</sub>= lightest grey; holes are black. Scale 1:650, oil immersion.
- Fig. 3. Oroya high temperature roasted zinc pellet ( $\pm 1050^{\circ}$  C). Scale 1:150; typical layered concentric structure with layers rich in zincite, in magnetite, or in holes, respectively. Towards the outside the amount of magnetite (or franklinite) is clearly decreasing.
- Fig. 4. Enlarged part of such a pellet (scale 1:600, oil immersion), exhibiting the grain shape and size, and the arrangement in layers.
- Fig. 5. Roasted zinc pellet: Oroya high temperature calcine ( $\pm 1050^{\circ}$  C). Coarse grained center portion re-crystallization has produced a granular agglomeration of ZnO (dark grey) and Fe<sub>3</sub>O<sub>4</sub> (light grey). Scale 1:650. Oil immersion
- Fig. 6. High temperature agglomerated pellets. Strong concentration of zoned spinels, consisting of about Fe<sub>3</sub>O<sub>4</sub> inside (light grey) and ZnFe<sub>2</sub>O<sub>4</sub> outside, (franklinite, grey rims). There are a few ZnO grains between the spinels. Black bakelite as matrix. Scale 1:650. Oil immersion.



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35—50% Fe-oxide and Zn-ferrites 50—65% ZnO

Magnetic separation, as praticed by certain zinc smelters, depends upon the grain size of the re-crystallized pellets. Also, according to data found in the literature, the magnetic susceptibility of franklinite appears to vary in a wide range.

A comparison with the Franklin, New Jersey Zinc deposits suggests the possibility of a similarity between the processes that lead to these zincite-franklinite-magnetite deposits and the metamorphism during roasting of zinc pellets. In the ore metamorphism inside the earth's crust oxygen has to be furnished, of course, by some chemical process, Brown (1950, p. 177) mentions the possibility that, "probably by reaction with the limestone, some zinc silicate may have been reduced to zinc oxide".

### Acknowledgement

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