A Mineralogical Study of the Reductive Roasting of Zinc Ferrite Residues—A Potential Zinc Recycling Technology

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A stockpiled zinc ferrite residue from Noranda Inc., CEZInc consists mostly of ZnFe$_2$O$_4$ and Fe$_2$O$_3$, together with trace amounts of a number of other phases including Mn-bearing oxides and Sr sulphate. Reductive roasting of the zinc ferrite residue for 2 h at 800°C resulted in the extensive conversion of the ZnFe$_2$O$_4$ to (Fe, Zn)O and ZnO; the (Fe, Zn)O phase contains about 16 mass%Zn. The particle sizes and shapes after reductive roasting are similar to those in the unroasted feed, but the roasted material may be slightly more porous. The copper impurity in the ferrite residue is reduced to an Ag-bearing copper alloy which occurs as inclusions along the grain boundaries of the (Fe, Zn)O phase. Some of the Sr sulphate present in the zinc ferrite residue is reduced to a Zn-Fe-Sr sulphide phase, and all of the initially present Fe$_2$O$_3$ is reduced to (Fe, Zn)O. Reductive roasting converts the zinc ferrite residue into species which are soluble in dilute acid or alkaline media, thereby allowing the potential recycling of the Zn, Cu and Ag values.

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1. Introduction

The majority of the world’s zinc is produced by the roast-leach-electrowinning process, in which zinc sulphide concentrates are roasted in air to convert them to an acid-soluble oxide form. Although most of the zinc present in the concentrates is roasted to ZnO, some reacts with the iron in the concentrate to form zinc ferrite, ZnFe$_2$O$_4$. The ZnO is readily soluble in dilute acid media, whereas the zinc ferrite requires hot concentrated acid to effect its dissolution. The strongly acid conditions result in the dissolution of the associated iron, which must subsequently be precipitated in an easily filterable form. Although the development of the jarosite, goethite and hematite technologies permits the effective precipitation of the iron, all three processes generate voluminous residues which must be discarded in an environmentally acceptable manner.1

As noted above, the jarosite, goethite and hematite technologies allow the iron dissolved during hot acid leaching to be effectively precipitated. However, some operations do not use hot acid leaching and continue to generate zinc ferrite residues. In addition, some operations have accumulated zinc ferrite residues from pre-hot acid leaching operations, and similar materials are generated in other metallurgical processes. It would clearly be desirable to develop innovative technologies to allow all of these materials to be recycled without generating large tonnages of iron residue for disposal. One of the promising options is reductive roasting, possibly using innovative technologies such as the expanded TORBED reactor.2

In order to evaluate the efficiency of the operation and to understand the fundamental chemical reactions taking place during the reductive roasting of such zinc-containing materials, a mineralogical study of the stockpiled zinc ferrite residue at Noranda Inc., CEZInc and of the same residue after reductive roasting was carried out. The zinc ferrite residue had been generated in the CEZInc weak acid leach circuit prior to the installation of simultaneous hot acid leaching-jarosite precipitation technology (the jarosite conversion process) in 1970. Presently, about 760,000 tonnes of this material are stored in a pond adjacent to the zinc plant, and the ponded material is a significant Zn, Cu and Ag resource.3,4 Accordingly, the overall objective of the present study was to ascertain whether reductive roasting transformed the stockpiled zinc ferrite residue into a material from which the Zn, Cu and Ag values could be recycled using various established techniques.5,6 The results of the mineralogical study of the stockpiled zinc ferrite residue and the material after reductive roasting, together with a general discussion of the recyclability of the reductively roasted material, are given in this report.

2. Experimental

A stockpiled zinc ferrite residue and the same residue after reductive roasting in a laboratory reactor were studied. The zinc ferrite residue was supplied by Noranda Inc., CEZInc and it contained 16.6 mass%Zn, 36.1 mass%Fe and 0.61 mass%Cu. The reductive roasting was done at Process Research ORTECH. The residue was treated for 2 h at 800°C in a gas stream containing 40 vol%CO and 60 vol% CO$_2$. The reductively roasted material contains 17.1 mass%Zn, 38.3 mass%Fe and 0.71 mass%Cu.

Polished section mounts of the as-received samples were prepared, and the polished sections were analyzed by optical microscopy, by scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX), and by electron microprobe analysis to determine the mineral species, their chemical compositions and their microstructures. To complement the mineral identifications, the as-received materials were also studied by X-ray powder diffraction (XRD) analysis to identify the major crystalline phases. Details of the mineralogical procedures are available in the literature.7
3. Results and Discussion

3.1 CEZinc stockpiled zinc ferrite residue

X-ray diffraction analysis indicates the presence of a major amount of ZnFe$_2$O$_4$, a minor amount of Fe$_2$O$_3$, and trace quantities of gypsum, sphalerite, talc (Fe–Mg silicate) and likely also Fe$_3$O$_4$. Figure 1 shows the general morphology of the sample. The compact grains are mainly ZnFe$_2$O$_4$ (lighter) and Fe$_2$O$_3$ (slightly greyish). The porous grains are mainly Fe$_2$O$_3$ mixed with ZnFe$_2$O$_4$ and Fe$_3$O$_4$; the compact rims on the porous grains are ZnFe$_2$O$_4$ and Fe$_2$O$_3$. The bright grains are unreacted sphalerite. The particles are crudely spherical in shape, and in this field of view, the particle sizes mainly range between 30 to 60 μm. The stockpiled zinc ferrite residue consists of major amounts of ZnFe$_2$O$_4$ and a minor amount of Fe$_2$O$_3$, in addition to trace quantities of Fe$_2$O$_3$, SrSO$_4$, (Pb, Sr)SO$_4$, Fe–Zn sulphate, Mn–Fe oxide, Mn oxide, gypsum, talc (Fe–Mg silicate), Zn$_2$SiO$_4$, quartz, Fe–Mg–Mn silicate, Fe–Mg–Al silicate, Ca–Na–Al silicate, SnO$_2$, Fe–Zn–Mg–Al silicate, Fe–Zn–Pb silicate, Na–Mg–Al–Fe–Zn silicate, sphalerite, Mn–Fe silicate and Fe oxide (hydroxide?). Figure 2 shows the morphologies of some of these species. Among these species, ZnFe$_2$O$_4$, Fe$_3$O$_4$, SnO$_2$, sphalerite, (Mn, Fe)$_2$O$_3$, Zn$_2$SiO$_4$, quartz, talc and all the silicates are residual calcine particles from the roasting of zinc concentrates in the CEZinc operation. In contrast, the SrSO$_4$, (Pb, Sr)SO$_4$, Mn oxide, Mn–Fe oxide, Mn–Fe–Pb oxide, Fe–Zn sulphate, Fe oxide (hydroxide?), PbSO$_4$ and gypsum are compounds generated during the leaching or electrowinning processes in the zinc plant. The particle sizes of the ferrite residue vary from approximately 1 to 70 μm; however, a few particles are as fine as ~1 μm. The residual calcine particles are coarser in size, usually > 25 μm, whereas the precipitates generated during leaching or electrorefining are usually finer, mainly < 20 μm.

Most of the particles in the ferrite residue are porous, crudely spherical, and approximately 40 to 60 μm in size, which corresponds to the particle size range of the zinc concentrate. Most of the porous cores consist of Fe$_2$O$_3$ (slightly darker), ZnFe$_2$O$_4$ (lightest) and Fe$_3$O$_4$ (lighter); the relatively compact rims (light) are ZnFe$_2$O$_4$. Some of the particles consist of a porous Fe$_2$O$_3$ core and a ZnFe$_2$O$_4$ rim, or of a Fe$_2$O$_3$ core (darker) and a Fe$_3$O$_4$ rim (lighter). These particles are believed to have formed during the oxidative roasting of pyrite or pyrrhotite grains in the CEZinc roaster circuit. Presumably the porosity of the grains was caused by the evolution of SO$_3$ during roasting or by the volume differences of the various reaction products. Most of the compact grains are Fe$_3$O$_4$ which have a ZnFe$_2$O$_4$ rim (Fig. 1); they likely formed from the reaction of zinc oxide fume and oxygen with the magnetite particles during the oxidative roasting of the zinc concentrate. It is common that compact Fe$_2$O$_3$ rims form on the surfaces of porous Fe$_2$O$_3$ grains during roasting. It can be deduced from the morphology of the calcine particles (Fig. 2) that, as the roasting time increases, more porous Fe$_2$O$_3$ or Fe$_3$O$_4$ particles will likely react to form ZnFe$_2$O$_4$. The reaction begins at the surfaces of the particles and proceeds inward.

Most of the ZnFe$_2$O$_4$ occurs as coarse (20–60 μm) compact grains, as compact grains with minor porosity (Figs. 1 and 2) and as intergrowths with Fe$_2$O$_3$ or Fe$_3$O$_4$ in porous grains. A small amount is present as compact rims on the porous Fe$_2$O$_3$ or Fe$_3$O$_4$ particles (Fig. 2). Well formed tiny ZnFe$_2$O$_4$ crystals are commonly detected in the fine-grained (< 3 μm) portion of the sample, but are also present in the porous particles. Figure 3 illustrates three porous ZnFe$_2$O$_4$ particles which consist of tiny intergrown crystals of ZnFe$_2$O$_4$. Presumably, the voids in the upper-right and the lower-left particles were originally filled by ZnO prior to leaching in the zinc plant. Electron microprobe analyses were carried out on the ZnFe$_2$O$_4$ particles, and the results are reported in Table 1. The average analyses give (in mass%): Zn 24.48, Fe 46.82, Cu 1.35, Pb 0.08, Mn 0.21 and Si 0.02. Noticeable is the presence of trace amounts of Cu, Pb, Mn and Si in the ZnFe$_2$O$_4$ structure. A minor amount of Fe$_3$O$_4$ is present in the stockpiled zinc ferrite residue. The Fe$_3$O$_4$ occurs mainly as compact grains; only a trace amount is detected in the intergrowths with Fe$_2$O$_3$ or ZnFe$_2$O$_4$ in the porous grains (Figs. 1 and 4). Table 1 shows that the Fe$_3$O$_4$ phase contains trace amounts of Zn (0.39 mass%) and Si (0.09 mass%). A signif-
significant amount of Fe₂O₃ is detected in the zinc ferrite residue; the Fe₂O₃ occurs mainly as the porous cores of large particles, and it commonly exhibits a compact rim of ZnFe₂O₄ or FeO₂. Table 1 also lists the average composition of the FeO₂ phase, which contains trace amounts of Zn, Cu, Mn, Si and Pb. From a recycling perspective, the significant Cu contents of the ZnFe₂O₄ and Fe-Zn-Mn oxide phases are of interest.

Figure 3 also shows several particles of SrSO₄, Mn–Fe–Zn oxide, Mn–Fe–Si oxide and Mn oxide; the Mn–Fe–Si oxide phase appears to be a precipitated compound. The strontium compounds originate from the SrCO₃ which is added to the zinc electrowinning circuit to control soluble lead. The manganese phases originate from the Mn oxide scale formed on the lead anodes during zinc electrowinning; the Mn oxide scale is recycled, as an oxidant, to the leaching circuit in the zinc plant. The Mn–Zn–Fe oxide, Mn oxide, Mn–Fe oxide, SrSO₄ and (Pb, Sr)SO₄ occur in trace quantities as small compact grains in the stockpiled zinc ferrite residue. The Fe–Zn–Mn oxide phase contains (in mass%): Mn 10.46, Fe 29.20, Zn 18.22, Cu 1.28, Pb 0.59 and Si 1.20 (Table 1).

The SrSO₄ and (Pb, Sr)SO₄ phases occur as small (10 to 15 μm) compact particles. Electron microprobe analyses were carried out on these particles, and the results are given in Table 2. The SrSO₄ phase contains a minor amount of Pb, and the (Pb, Sr)SO₄ phase contains a major amount of Sr. Lead and strontium substitute for each other in the sulphate phases because the two compounds are isostructural and because the lead and strontium ions have similar radii. The SrSO₄ and (Pb, Sr)SO₄ phases contain small amounts of Fe, Zn, Cu and Mn.

A trace amount of Zn₂SiO₄ is present in the stockpiled zinc ferrite residue. The Zn₂SiO₄ occurs as compact grains which commonly contain tiny inclusions of ZnFe₂O₄ and FeO₂ (Fig. 4); it also occurs as a reaction rim on quartz and silicate particles. It is rarely detected as tiny grains in porous particles of FeO₂ + ZnFe₂O₄. A small amount occurs as tiny grains in the fine-grained (< 3 μm) portion of the sample. These tiny grains likely originated from the Zn₂SiO₄ inclu-sions present in the agglomerated ZnO masses in the original roaster calcine. The average electron microprobe analyses of the Zn₂SiO₄ phase are (in mass%): Zn 51.43, Fe 4.24, and Si 13.29.

Table 2 Average electron microprobe analyses of the SrSO₄ and (Pb, Sr)SO₄ phases in the CEZine stockpiled zinc ferrite residue (mass%).

<table>
<thead>
<tr>
<th></th>
<th>SrSO₄</th>
<th>(Pb, Sr)SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>42.84</td>
<td>17.27</td>
</tr>
<tr>
<td>S</td>
<td>15.57</td>
<td>13.27</td>
</tr>
<tr>
<td>Pb</td>
<td>2.26</td>
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<tr>
<td>Fe</td>
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<tr>
<td>Zn</td>
<td>2.41</td>
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<tr>
<td>Cu</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>Mn</td>
<td>0.10</td>
<td>0.07</td>
</tr>
</tbody>
</table>

3.2 Reductively roasted zinc ferrite residue

The CEZine stockpiled zinc ferrite residue was roasted for 2 h at 800°C under a reducing atmosphere composed of 40 vol% CO + 60 vol% CO₂. The reductively roasted material contains 17.1 mass%Zn, 38.3 mass%Fe and 0.71 mass%Cu. X-ray diffraction analysis of the reductively roasted product indicates the presence of a major amount of FeO, a minor amount of ZnO, and trace quantities of ZnFe₂O₄, quartz, sphalerite and Zn₂SiO₄. Comparison with the material prior to reductive roasting indicates that reduction of the ZnFe₂O₄ and Fe₂O₃ to form FeO and ZnO has occurred. Figure 5 shows the general morphology of the reductively roasted
product. The sizes and shapes of the particles are essentially identical to those prior to roasting; however, the compositions of the particles have changed from ZnFe$_2$O$_4$, Fe$_3$O$_4$ and Fe$_2$O$_3$ to FeO, (Fe, Zn)O and ZnO. In Fig. 5, the dominant light grey particles are FeO which contains trace inclusions of ZnO; the dark grey particles with light rims are Zn–Fe–Mn oxide cores with ZnO rims, and the small light grains are SrSO$_4$ cores with Zn–Fe–Sr sulphide rims. A porous Fe–Mg–Al silicate, similar to that shown in Fig. 4, is evident at the left side of the photomicrograph. Only a few particles still retain the ZnFe$_2$O$_4$ composition. In general, the reductively roasted product consists of major FeO, minor to trace amounts of ZnO, ZnFe$_2$O$_4$, Fe$_3$O$_4$, Zn–Fe–Mn oxide, Fe–Cu–Zn oxide, SrSO$_4$ and Zn–Fe–Sr sulphide, together with trace quantities of Cu alloy, Fe–Sb alloy, sphalerite, Zn$_2$SiO$_4$, quartz, SnO$_2$, Fe–Cu–Mg–Al–K silicate, Zn–Fe sulphate and Al–Mg–K silicate. The reductively roasted product appears to be slightly more porous than the original un-roasted material. The main difference between the roasted and the un-roasted material is that the original ZnFe$_2$O$_4$, Fe$_3$O$_4$ and Fe$_2$O$_3$ phases have been converted, or partially converted, to FeO or (Fe, Zn)O and a Zn-rich (Zn, Fe)O phase. The implication is that the zinc has been converted to a readily soluble form that could greatly facilitate its recycling within the industry. The trace impurities, such as Cu, Ag and Sn, which were originally present in the ZnFe$_2$O$_4$, Fe$_3$O$_4$ and Fe$_2$O$_3$ phases, were converted to Cu alloys having (Cu, Fe, Sn), (Cu, Fe, Zn) and (Cu, Fe, Sn, Ag) compositions.

The ZnO phases produced during reductive roasting still retain the morphology of the original particles. Figure 6 shows the detailed morphology of a typical (Fe, Zn)O particle in the sample. The particle consists of (Fe, Zn)O (grey matrix) and a minor amount of ZnO (light), which occurs as hairline-like particles along the (Fe, Zn)O grain boundaries. Presumably, the entire particle was ZnFe$_2$O$_4$ or (Fe, Zn)$_2$O$_3$ prior to reductive roasting. Traces of tiny (Cu, Fe, Sn) alloy, (Cu, Fe, Zn) alloy and (Cu, Fe, Cd, Pb, Sn) alloy particles are present in the (Fe, Zn)O matrix. The (Cu, Fe, Zn) alloy and the (Cu, Fe, Sn) alloy also occur along the (Fe, Zn)O grain boundaries. The occurrence of ZnO and Cu alloys along the FeO or (Fe, Zn)O grain boundaries implies that these phases formed from the impurities in the ZnFe$_2$O$_4$ or Fe$_3$O$_4$ compounds during reductive roasting, when the ZnFe$_2$O$_4$ or Fe$_3$O$_4$ were converted to FeO or (Fe, Zn)O.

\[
\text{ZnFe}_2\text{O}_4 + \text{CO} \rightarrow 2\text{FeO} + \text{ZnO} + \text{CO}_2
\]

\[
\text{ZnFe}_2\text{O}_4 + \text{CO} \rightarrow 2(\text{Fe}_{1-x}\text{Zn}_x)\text{O} + (\text{Zn}_{1-y}\text{Fe}_y)\text{O} + \text{CO}_2
\]

\[
(\text{Zn}_{1-x}\text{Cu}_x)\text{Fe}_2\text{O}_4 + (2 + x)/2\text{CO}
\]

\[
\rightarrow 2\text{FeO} + (1 - x)\text{ZnO} + x\text{Cu} + (2 + x/2)\text{CO}_2
\]

\[
\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2
\]

\[
(\text{Fe}_{1-x-y}\text{Cu}_x\text{Zn}_y)\text{O}_2 + (1 + 3x + 3y)\text{CO}
\]

\[
\rightarrow 3\text{Fe}_{1-x-y}\text{O}_{1+y-x-y} + 3(\text{Cu}_y\text{Zn}_{1-y}) + (1 + 3x + 3y)\text{CO}_2
\]

Figure 7 suggests that all the (Fe, Zn)O particles in the sample, regardless of whether they are porous or compact, contain ZnO and Cu alloy inclusions along the grain boundaries. This implies that the porous Fe$_3$O$_4$ particles originally present in the zinc ferrite residue were also converted to FeO or (Fe, Zn)O; in fact, Fe$_2$O$_3$ was not detected in the reductively roasted sample:

\[
\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2
\]

Figures 6 and 7 indicate that FeO, or (Fe, Zn)O, is the dominant phase in the reductively roasted sample; it occurs as the matrix of both the compact grains and the porous particles. Table 3 summarizes the compositions of the (Fe, Zn)O phase, which vary from particle to particle and range from approximately FeO to Fe$_3$O$_4$ in composition. The average composition gives (in mass%): Fe 58.23, Zn 15.76, Cu 0.50, Mn 0.55 and Pb 0.29. X-ray diffraction analysis indicates that the reductively roasted zinc ferrite residue contains a dominant FeO phase and only trace quantities of ZnFe$_2$O$_4$ or Fe$_3$O$_4$, which are difficult to differentiate from each other because of the mutual substitution of Zn and Fe in the nearly identical
structures. Quantitative electron microprobe analyses, used in conjunction with the X-ray diffraction results, indicate that the (Fe, Zn)O particles likely consist of major FeO and trace ZnFe$_2$O$_4$ or Fe$_2$O$_3$. The FeO phase also contains a significant amount of Zn as well as trace quantities of Cu, Mn and Pb. Because of the intimate intergrowth of FeO, Cu alloy and ZnO, it is believed that a major portion of the detected Cu and Zn contents of the (Fe, Zn)O phase originates from the inclusions. Nevertheless, there is still a significant amount of Zn in solid solution in the FeO phase; hence, the composition is (Fe, Zn)O. Because Zn and Cu segregate from the FeO phase to form ZnO and Cu alloy along the FeO grain boundaries, longer roasting times might remove more Zn and Cu from the FeO phase and produce more ZnO and Cu alloy inclusions along the FeO grain boundaries.

Figure 8 shows a porous (Fe, Zn)O particle containing several tiny inclusions of (Cu, Fe, Zn, Sn) alloy. The abundance of (Cu, Fe, Zn, Sn) alloy particles suggests that not all of the Cu, Sn and Zn in the Cu alloy originated from the solid solution impurities in the ZnFe$_2$O$_4$, Fe$_2$O$_3$ or Fe$_3$O$_4$ phases. In this regard, Fig. 9 shows several ~5 µm spheroids of (Cu, Fe, Sn) alloy occurring as discrete particles or adhering to sphalerite grains. The spherical morphology implies that these particles originated from condensed fume. Electron microprobe analyses were carried out on the large spheroidal Cu alloy particles and the results are given in Table 4. The Cu alloy contains a major amount of Sn and minor amounts of Fe, Zn and Ag; it has the general composition of (Cu, Fe, Sn, Zn, Ag). The preferential concentration of Ag in the copper alloy phases might allow its recovery in a subsequent recycling operation. The Sn appears to be a common constituent of the Cu alloys. However, because the SnO$_2$ phase in the sample appears to be largely unaffected by reductive roasting, it is probably not the only source of Sn for the (Cu, Fe, Sn) alloy.
Table 5 Electron microprobe analyses of the Fe–Mn–Zn oxide, the Fe–Zn–Cu oxide, the Zn–Cu–Fe oxide and the associated ZnO phase in the reductively roasted zinc ferrite residue (mass%).

<table>
<thead>
<tr>
<th></th>
<th>Fe–Mn–Zn oxide core</th>
<th>Fe–Mn–Zn oxide core</th>
<th>ZnO rim</th>
<th>ZnO rim</th>
<th>Fe–Zn–Cu oxide</th>
<th>Zn–Cu–Fe oxide</th>
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<tr>
<td>Fe</td>
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<td>32.03</td>
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</table>

Fig. 10 Backscattered electron image showing a Fe–Mn–Zn oxide particle with a ZnO rim (bright) in the reductively roasted zinc ferrite residue. 1–Fe–Mn–Zn oxide, 2–ZnO rim, 3–(Fe, Zn)O, 4–sphalerite.

Also present in trace amounts in the reductively roasted zinc ferrite residue is a (Fe, Cu, Zn, Pb, Cd) alloy phase (Fig. 6) which occurs as tiny particles at the grain boundaries of the (Fe, Zn)O phase. Electron microprobe analyses of the larger particles indicate that this phase contains major amounts of Cu (20 mass%), Fe (24 mass%), Zn (8 mass%), Cd (20 mass%) and Pb (18 mass%), as well as trace amounts of Mn (0.2 mass%). It is believed to be an alloy phase and likely originated from inclusions in the ZnFe₂O₄.

Electron microprobe analyses were also carried out on the hairline-like ZnO phase which is present in almost all the (Fe, Zn)O particles. Because of the tiny (< 1 µm) particle sizes, only qualitative analyses were obtained. Nevertheless, the analyses show major amounts of Zn (~60 mass%) and Fe (~20 mass%), together with trace quantities of Cu, Mn and Pb. The observed Fe content is believed to arise mostly from the adjacent (Fe, Zn)O phase. The oxide is the only Zn-rich phase detected in the sample, and its presence was confirmed by X-ray diffraction analysis. The ZnO phase formed through the reduction of zinc ferrite. However, a trace amount of the ZnO appears to have formed by the reaction of Zn vapour or ZnO fume with Fe–Mn–Zn oxide. In this regard, Fig. 10 shows a Fe–Mn–Zn oxide particle with a ZnO rim. The Fe–Mn–Zn oxide phase is present in trace amounts in the sample, and it occurs as porous grains with thin rims which have a high Zn content. Some of the particles are clearly rimmed with ZnO, as is illustrated in Fig. 10. The compact and sharp contact between the ZnO rim and the Fe–Mn–Zn oxide core likely implies that the rim formed through the reaction of Zn vapour or ZnO fume with Fe–Mn–Zn oxide, rather than by the diffusion of ZnO from the Fe–Mn–Zn oxide core to the surface of the particle. Table 5 summarizes the compositions of some of these particles. Likely, a major portion of the detected Fe and Mn contents of the ZnO rims originates from secondary X-ray fluorescence of the associated Fe–Mn–Zn oxide core; that is, the rim is often ZnO, a conclusion supported by X-ray concentration mapping for Zn, Fe and Mn.

Trace amounts of a Fe–Zn–Cu oxide phase and a Zn–Cu–Fe oxide phase are present in the reductively roasted sample; they have similar morphologies to those of the Fe–Mn–Zn oxide phase. The analyses of these oxide phases are also given in Table 5.

Another interesting reaction occurring during reductive roasting is the conversion of SrSO₄ to a Zn–Fe–Sr sulphide phase on the periphery of the SrSO₄ particles. Many SrSO₄ particles with Zn–Fe–Sr sulphide rims are present in the reductively roasted sample. The sizes of the SrSO₄ particles vary from 10 to 50 µm, and the Zn–Fe–Sr sulphide rims range from 2 to 10 µm in thickness. Although none of the SrSO₄ particles was totally converted to Zn–Fe–Sr sulphide, most of the smaller particles were extensively reacted. Figure 11 shows several such particles exhibiting a morphology consisting of SrSO₄ cores and Zn–Fe–Sr sulphide rims. Many of the smaller SrSO₄ particles are almost completely converted to the Zn–Fe–Sr sulphide phase. The identification of a sulphide species, as opposed to a sulphate species, was done by the SKα X-ray line spectrometer position of the Zn–Fe–Sr sulphide phase. Furthermore, the Zn–Fe–Sr sulphide phase fluoresces under electron beam bombardment, and such fluorescence is typical of most Zn sulphide species. The morphologies of the SrSO₄ particles are essentially the same as those in the unroasted material, except that the reductively roasted SrSO₄ particles may be slightly more porous. Electron microprobe analyses were carried out on the SrSO₄ particles, and on the Zn–Fe–Sr sulphide rims, and the results are given in Table 6. The SrSO₄ phase contains minor to trace amounts of Pb, Zn, Fe, Cu and Mn, whereas the Zn–Fe–Sr sulphide phase contains minor amounts of Pb and Cu, as well as a trace of Mn. In comparison to the composition of the SrSO₄ phase prior to reductive roasting (Table 2), the SrSO₄ cores of the reductively roasted material show a significant decrease in their Pb, Fe and Zn contents, and an increase in the Sr content. In contrast, the Zn–Fe–Sr sulphide rims have higher Pb, Fe and Zn contents, but lower Sr contents. This implies that Pb, Fe and Zn diffused from the core to the
to that of stoichiometric ZnFe$_2$O$_4$ (Zn 27.12 mass% and Fe 46.33 mass%). The ZnFe$_2$O$_4$ phase contains trace amounts of Cu, Mn and Pb. As compared to the composition of the ZnFe$_2$O$_4$ phase prior to reductive roasting (Table 1), the Cu content has been reduced significantly, because the Cu segregated from the zinc ferrite structure to form various Cu alloys.

A trace amount of Fe$_2$O$_3$ or (Fe, Zn, Mn)$_2$O$_4$ is present in the reductively roasted sample, and Fig. 11 shows two such particles. Both Fe$_2$O$_3$ and (Fe, Zn, Mn)$_2$O$_4$ occur as compact grains in the photomicrograph. The Fe$_2$O$_3$, (Fe, Zn, Mn)$_2$O$_4$, ZnFe$_2$O$_4$ and (Zn, Fe, Mn)Fe$_2$O$_4$ have similar structures and differ only in composition.

4. Conclusions

The CEZinc stockpiled zinc ferrite residue consists of major amounts of ZnFe$_2$O$_4$ and a minor amount of Fe$_2$O$_3$, together with trace quantities of Fe$_2$O$_3$, SrSO$_4$, (Pb, Sr)SO$_4$, Fe–Zn sulphate, Mn–Fe oxide, Mn oxide, gypsum, talc, Zn$_2$SiO$_4$, quartz, Fe–Mg–Mn silicate, Fe–Mg–Al silicate, Ca–Na–Al silicate, SnO$_2$, Fe–Zn–Mg–Al silicate, Fe–Zn–Pb silicate, Na–Mg–Al–Fe–Zn silicate, sphalerite, Mn–Fe silicate and Fe oxide (hydroxide?). Among these species, Zn$_2$SiO$_4$, Fe$_2$O$_3$, Fe$_3$O$_4$, SnO$_2$, sphalerite, (Mn, Fe)$_2$O$_4$, Zn$_2$SiO$_4$, quartz, talc and other silicates are residual calcine products from the CEZinc roasting operation, whereas SrSO$_4$, (Pb, Sr)SO$_4$, Mn oxide, Mn–Fe oxide, Mn–Fe–Pb oxide, Fe–Zn sulphate, Fe oxide (hydroxide?), PbSO$_4$ and gypsum are compounds generated during the leaching or zinc electrowinning processes. The particle sizes of the ferrite residue range from approximately 1 to 70 μm, with most particles occurring between 30 to 60 μm; a few particles are as small as ~1 μm. The residual calcine particles are coarser, usually > 25 μm, whereas the leaching or electrowinning precipitates are usually finer, mainly < 20 μm in size. The residual calcine particles are crudely spherical in shape; approximately one-third occurs as compact grains, and the remainder is present as porous grains. The compact grains are mostly ZnFe$_2$O$_4$ and silicates, together with trace amounts of sphalerite, Fe$_2$O$_3$, quartz and Zn$_2$SiO$_4$. The porous particles are mainly Fe$_2$O$_3$, together with minor ZnFe$_2$O$_4$, Fe$_3$O$_4$, Zn$_2$SiO$_4$ and some Fe–Mg–Al silicate. The zinc ferrite, Fe$_2$O$_3$ and Fe$_2$O$_4$ phases contain trace amounts of Cu, Pb, Mn, Zn and Si.

Roasting of the zinc ferrite residue for 2 h at 800°C under a reducing atmosphere composed of 40 vol% CO + 60 vol% CO$_2$ resulted in a product consisting of a major amount of (Fe, Zn)O, minor to trace amounts of ZnO, ZnFe$_2$O$_4$, Fe$_3$O$_4$, Zn–Fe–Mn oxide, Fe–Cu–Zn oxide, SrSO$_4$ and Zn–Fe–Sr sulphide, together with trace quantities of Cu alloy, Fe–Sb alloy, sphalerite, Zn$_2$SiO$_4$, quartz, SnO$_2$, Fe–Ca–Mg–Al–K silicate, Zn–Fe sulphate and Al–Mg–K silicate. The particle sizes and shapes are similar to those of the original zinc ferrite residue; however, the roasted particles appear to be slightly more porous. The ZnFe$_2$O$_4$, Fe$_2$O$_3$ and Fe$_2$O$_4$ phases in the original zinc ferrite residue were converted to (Fe, Zn)O and a low-Fe (Zn, Fe)O phase, likely ZnO, in the roasted product. The trace impurities such as Cu, Ag and Sn, originally present in the ZnFe$_2$O$_4$, Fe$_2$O$_3$ and Fe$_2$O$_4$ phases, were converted to Cu alloys of (Cu, Fe, Zn), (Fe, Cu, Zn, Pb, Cd), (Cu, Fe, Sn)

<table>
<thead>
<tr>
<th>SrSO$_4$ core</th>
<th>Zn–Fe–Sr sulphide rim</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
</tr>
<tr>
<td>Sr</td>
<td>46.09</td>
</tr>
<tr>
<td>Pb</td>
<td>1.44</td>
</tr>
<tr>
<td>Fe</td>
<td>0.86</td>
</tr>
<tr>
<td>Zn</td>
<td>1.79</td>
</tr>
<tr>
<td>Cu</td>
<td>0.06</td>
</tr>
<tr>
<td>Mn</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Fig. 11 Backscattered electron image showing the morphology of the SrSO$_4$ phase in the reductively roasted zinc ferrite residue. 1-SrSO$_4$ core, 2-Zn–Fe–Sr sulphide (rim, bright), 3-ZnFe$_2$O$_4$, 4-(Fe, Zn, Mn)$_2$O$_4$, 5-(Fe, Zn)O.
and (Cu, Fe, Sn, Ag) composition. The resulting (Fe, Zn)O
phase retains the morphology of the original particles and
contains a significant amount of Zn (15.76 mass% Zn). This
(Fe, Zn)O phase commonly occurs as the matrix of the par-
ticles, and minor amounts of ZnO, occurring as hairline-like
inclusions, and of Cu alloys, occurring as tiny particles along
the grain-boundaries of the (Fe, Zn)O phase, are detected in
the matrix. The Fe₂O₃ phase, originally present in the fer-
rille residue, is absent in the reductively roasted product. The
ZnFe₂O₄ phase, which is dominant in the zinc ferrite residue,
is present only in trace quantities in the roasted product. Not
all the ZnO in the reductively roasted product originated from
the reduction of ZnFe₂O₄; a trace amount appears to have
formed by the reaction of Zn vapour or ZnO fume with Fe–
Zn–Mn oxide. The conversion of sulphate phases to sulphide
phases also takes place during reductive roasting. A small
amount of SrSO₄ phase is present in the zinc ferrite residue;
during reductive roasting, the peripheries of the SrSO₄ par-
ticles were converted to a Zn–Fe–Sr sulphide phase which pre-
served the morphology of the original SrSO₄ particles. The
Zn and Fe in the Zn–Fe–Sr sulphide phase appear to have
originated from the vapour phase or from adjacent ZnFe₂O₄
grains.

Reductive roasting of zinc ferrite residues, and presum-
ably of similar zinc-containing materials, converts the refrac-

tory ZnFe₂O₄, Fe₂O₃ and Fe₃O₄ phases into more reactive
(Fe, Zn)O and ZnO compounds. These latter phases are read-

ily soluble in dilute acid or in alkaline media. Once dissolved,
the zinc values could be readily recycled using a number of
established technologies. Reductive roasting also converts
most of the copper in the zinc ferrite residue into various

copper alloys, which also collect the contained silver val-

ues. Consequently, hydrometallurgical processing of the re-

ductively roasted material should also permit the recycling of
both the copper and silver values.

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