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## **MINERALOGY AND SILVER DISTRIBUTION IN ARGENTIFEROUS MANGANESE ORES FROM LA ENCANTADA MINES IN MEXICO**

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**Abstract:** Various Ag-Mn ore samples from La Encantada Mines in Mexico, were mineralogically characterized by XRD, SEM and TEM. The major minerals in the ore samples were found to be calcite ( $\text{CaCO}_3$ ), pyrosulite ( $\text{MnO}_2$ ), johannsenite ( $\text{CaMn}(\text{Si}_2\text{O}_6)$ ), quenselite ( $2\text{PbO}\cdot\text{Mn}_2\text{O}_3\cdot\text{H}_2\text{O}$ ), cerussite ( $\text{PbCO}_3$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ). TEM studies revealed no silver in the crystal lattice of the manganese oxides neither in their pores. SEM showed silver in the ore as native silver (Ag), acanthite ( $\text{Ag}_2\text{S}$ ), cerargyrite ( $\text{AgCl}$ ), embolite ( $\text{Ag}(\text{Cl},\text{Br})$ ) and freibergite ( $(\text{Ag},\text{Fe},\text{Zn},\text{Cu})_{12}\text{Sb}_2\text{S}_{13}$ ). These Ag minerals with a size of less than 5  $\mu\text{m}$  were found to be occluded in the manganese oxides and hematite. Silver recovery by cyanide leaching was evaluated for the as-received ore samples and the samples free of carbonates, manganese oxide and iron oxides. The silver distribution in these mineral components of the ores was determined by selective leaching. Silver was found to be mostly distributed in manganese oxides with a lesser percentage in  $\text{Fe}_2\text{O}_3$  and  $\text{CaCO}_3$ . Very low silver recovery resulted from the as-received samples because of a high encapsulation level of the silver minerals in the manganese oxides and  $\text{Fe}_2\text{O}_3$ . Silver recovery significantly improved through fine grinding of the ore samples and dissolution of the manganese oxides from the samples.

**Keywords:** *silver manganese ores, silver, recovery, mineralogy, selective leaching*

### **Introduction**

Either direct flotation or cyanide leaching of Ag-Mn ores usually results in very low silver recovery because silver is either encapsulated or present in the crystal lattice of manganese oxides in the ores (Chase, 1981). To recover silver from these ores specialized extraction techniques are required. Simultaneous leaching of silver and

manganese was proposed using acidified thiourea (Pescic and Wey, 1986) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) combined with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (Jiang et al., 2003). These processes are very promising, however no industrial application has been reported so far. Industrial processes involve either hydro- or pyrometallurgical pretreatment of the Ag-Mn ores, where manganese is reduced to Mn(II) (Clevenger and Caron, 1925; Chase, 1981; Jiang et al., 2002, 2003). Hydrometallurgical pretreatments are based on (i) selective dissolution of the manganese oxides, which is achieved in acidic solutions of  $\text{SO}_2$  or  $\text{H}_2\text{SO}_3$ , and (ii) reduction of Mn(IV) to water soluble Mn(II) species. Miller and Wan (1983) showed that the dissolution rate of manganese dioxide ( $\text{MnO}_2$ ) was controlled by a surface chemical reaction. The dissolution rate for surface chemical reaction control was faster when compared to that for diffusion through the product layer control as in sulfuric acid leaching of zinc silicate ores (Abdel-Aal, 2000). Other lixivants have been proposed for the manganese oxides such as ammonium sulphite in the ammoniacal medium (Das et al., 1998), pyrite under mild acid conditions (Parida et al., 1990), sucrose, lactose and glucose in the acid media (Beolchini et al., 2001; Senanayake, 2003; Furlani et al., 2006) and corncob in sulfuric acid solutions (Ali et al., 2016). Bioleaching has also been proposed as an alternative method to leach the manganese oxides using the *bacterium thiobacillus ferroxidans* and *fungus aspergillus niger* (Abbruzzese et al., 1990). After dissolution of the manganese oxides, silver is recovered by cyanide leaching. The pyrometallurgical pretreatment involves either reductive or salt roasting (Clevenger and Caron, 1925; Chase, 1981). Through reductive roasting  $\text{MnO}_2$  is reduced to MnO, which is soluble in sulfuric acid solutions. Meanwhile, in the salt-roasting process AgCl is formed. The roasted ore is subjected to cyanide leaching for silver recovery. If the ore has copper minerals, a copper-silver alloy is formed in the roasting step. This alloy is recovered by flotation where a silver-copper concentrate is obtained.

Manganese occurs mainly as oxides in Ag-Mn ores (Gasparrini, 1993), such as pyrolusite ( $\text{MnO}_2$ ), polianite ( $\text{MnO}_2$ ), manganite ( $\text{Mn}^{3+}\text{O}(\text{OH})$ ), pyrochroite ( $\text{Mn}(\text{OH})_2$ ), backstromite ( $\text{Zn}_2\text{Mn}_4^{3+}\text{O}_8\cdot\text{H}_2\text{O}$ ) and psilomelane ( $(\text{Ba},\text{Mn}^{2+}\text{Mn}_8^{4+}\text{O}_{16}(\text{OH})_4)$ ), while the silver mineralogy was found to be very complex. In general, it has been reported that silver is mostly encapsulated or bound to the manganese oxides. Clevenger and Caron (1925) suggested that silver might occur as a manganese compound ( $\text{Ag}_2\text{MnO}_5$ ). Gasparrini (1993) reported silver as aurorite ( $\text{Ag},\text{Ba},\text{Ca},\text{Mn}^{2+}$ ) $\text{Mn}_3^{4+}\text{O}_7\cdot 3\text{H}_2\text{O}$ ). Hewitt (1968) and Siems (1967) proposed that silver was present in the crystal lattice replacing potassium atoms in cryptomelane ( $\text{K}(\text{Mn}_7^{4+}\text{Mn}^{3+})\text{O}_{16}$ ). Sorption studies showed that silver ions exchanged surface protons and most potassium ions in the cavity of the tunnel structure of cryptomelane (Ravikumar and Fuerstenau, 1996).

The aim of this work was to study the mineralogy and the silver distribution in the mineral components of various Ag-Mn ore samples from La Encantada Mines, located West from Rio Grande in Northeast Mexico. The ore contains abundant calcite ( $\text{CaCO}_3$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ) with lesser amounts of magnetite ( $\text{Fe}_3\text{O}_4$ ), goethite ( $\text{FeOOH}$ ), limonite ( $\text{FeOOH}\cdot n\text{H}_2\text{O}$ ), anglesite ( $\text{PbSO}_4$ ), cerussite ( $\text{PbCO}_3$ ) and zinc

silicates ( $\text{ZnSiO}_3$ ) (Anon, 1980). X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the ore samples.

## **Experimental**

### **Materials and equipment**

Silver-manganese ore samples were collected from La Encantada Mines. These samples were first crushed, then ground to  $P_{80}$  of 100  $\mu\text{m}$  for their mineralogical characterization by X-ray diffraction (XRD) and scanning electron microscopy (SEM), as well as for their elemental chemical analysis and valuation of the silver distribution in the various mineral components of the ore.

The XRD characterization was carried out in a Bruker diffractometer D8 Advance Da Vince using a copper cathode with a  $\lambda=0.15406$  nm. The SEM observations were performed using a JEOL JSM 6210LV, while transmission electron microscopy (TEM) was done with a JEOL JEM 1230 120 KV using an Oxford EDS. Atomic absorption spectrometry was used for the elemental chemical analysis of the ore samples, leached residues and silver in aqueous solutions.

All inorganic reagents used in this work were of analytical grade. They were sodium cyanide ( $\text{NaCN}$ ) and acetic ( $\text{CH}_3\text{COOH}$ ), sulfurous ( $\text{H}_2\text{SO}_3$ ) and hydrochloric ( $\text{HCl}$ ) acids. Lime ( $\text{CaO}$ ) was used as a pH regulator in cyanide leaching tests. All leaching tests were done with distilled water.

### **Experimental procedure**

The distribution of non-encapsulated and encapsulated silver in carbonate, manganese oxide and iron oxide minerals was determined in the Ag-Mn ores. Non-encapsulated silver was received by cyanide leaching. It was carried out by the roll-bottle procedure using 100 g sample and 500  $\text{cm}^3$  of an aqueous solutions with an initial  $\text{NaCN}$  concentration of 500  $\text{mg}/\text{dm}^3$  and pH 10.5-11. Lime was used to set the pH. During the cyanide leaching tests, pH was monitored every 12 h and adjusted back to its initial value. Moreover, 20  $\text{cm}^3$  aliquot was withdrawn from the pulp to determine the silver and free cyanide concentration in the pulp liquor. Sodium cyanide and make-up water were added to the pulp in order to reestablish the cyanide concentration to the initial values and to keep constant the volume of the aqueous solution in the pulp. Leaching was finished when the silver concentration in the liquor essentially did not change, meaning that no more silver leached out from the ore. This condition was reached in 72 h of leaching.

Encapsulated silver in carbonates was received by selective leaching of the carbonate using the acetic acid. Such selective leaching was carried out at 35 °C for 3 h with 250 g sample and 500  $\text{cm}^3$  of an aqueous solution with 10% acetic acid. This leaching step was repeated five-fold after which calcium ions were not detected in the

leached solution. The XRD analysis on the residues reported no carbonates. After filtration, the acid leached residue was dried at 60 °C for 24 h. A 100 g of this residue was cyanide leached following the procedure outlined above. Silver encapsulated in carbonates was calculated by subtracting silver extracted in this step, silver recovered in the direct cyanide leaching of the ore and using an appropriate mass balance for silver.

Silver encapsulated in the manganese oxides was received on samples that resulted from the removal of carbonates. A sample of 150 g was leached at 45 °C for 6 h in an aqueous solution with 15% H<sub>2</sub>SO<sub>3</sub> to selectively dissolve the manganese oxides of the ore. This treatment with H<sub>2</sub>SO<sub>3</sub> was carried out six-fold after which the manganese in the solid assayed about 0.3% Mn. After filtration, the residues of this H<sub>2</sub>SO<sub>3</sub> leaching step was dried at 60°C for 24 h. A 100 g of this residue was cyanide leached following the procedure outlined above. Silver encapsulated in the manganese oxides was calculated using an appropriate mass balance taking into account silver extracted in this step and the per cent of non-encapsulated and encapsulated silver in the carbonates.

Finally, silver encapsulated in iron oxides was received. It was effected on residues of the cyanide leaching step to find silver encapsulated in the manganese oxide. First, these residues were washed three-fold with a caustic aqueous solution to remove the liquor with cyanide and adsorbed silver ions. Then, the residues were treated with a 5% HCl aqueous solutions to dissolve the iron oxides. After filtration, the HCl-treated sample was dried and used for cyanide leaching. A 50 g of this dried sample was cyanide leached as outlined above. Silver encapsulated in the iron oxides was calculated from the silver recovery in this cyanide leaching step and mass balance on silver.

## Results and discussion

Table 1 shows the chemical analysis of the silver-manganese ore samples evaluated in this work. The Mn grade in the ores ranges from 2.2 to 12.3%, while Ag is from 144 to 1110 g/Mg. The content of Fe, Ca (reported as CaO), silica (SiO<sub>2</sub>), Pb and Zn in the ores was variable. The last column of Table 1 reports the Ag recovery from the ores by direct cyanide leaching. This silver recovery value is referred as the percentage of non-encapsulated Ag in the ores. It can be seen that the lower Ag recovery, the higher the Mn grade in the ore.

The mineral characterization was carried out by XRD and SEM on the as-received samples. XRD reported calcite (CaCO<sub>3</sub>), pyrolusite (MnO<sub>2</sub>), johannsenite (CaMn(Si<sub>2</sub>O<sub>6</sub>)), quenselite (2PbO·Mn<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O), hematite (Fe<sub>2</sub>O<sub>3</sub>), goethite (FeOOH), cerussite (PbCO<sub>3</sub>) as the major minerals. Quartz (SiO<sub>2</sub>), galena (PbS) and kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) were reported in minor quantities. All these minerals were also identified by SEM. Figure 1 shows SEM photomicrographs of the Mn oxides

pyrolusite, quenselite and johannsenite. It is noted that these minerals are highly porous.

Table 1. Grade of Ag, Mn, Pb, Zn, Fe, CaO and SiO<sub>2</sub> in the Ag-Mn ore samples from La Encantada Mines. Silver recovery by direct cyanide leaching of the samples is presented

Ag-Mn ore sample	Grade							Cyanide leach recovery
	g/Mg		%					%
	Ag	Mn	Pb	Zn	Fe	CaO	SiO <sub>2</sub>	Ag
A	144	2.2	3.1	4.4	28.2	4.3	20.9	56.7
B	276	4.8	2.0	0.9	16.8	37.8	5.1	11.0
C	319	5.5	2.4	1.3	26.6	12.9	4.1	25.4
D	138	8.7	2.2	1.0	29.3	8.9	5.8	15.4
E	1110	12.3	0.8	2.6	8.7	32.3	1.6	19.2

The distribution of Ag in carbonates, Mn oxides and Fe oxides in the ore samples is presented in Table 2. Non-encapsulated silver means Ag recovered by direct cyanide leaching of the ore. As seen, more than 50% of Ag is encapsulated in Mn oxides for the samples with the Mn grade higher than 2.2%. Only one sample showed about 20% of Ag occluded in Fe oxides. Ag encapsulated in carbonates is less than 4%.

Table 2. Non-encapsulated and encapsulated silver in manganese oxides, carbonates and iron oxide in Ag-Mn ores from La Encantada mines

Ag-Mn ore samples	Mn grade %	Silver distribution in Ag-Mn ore components, %			
		Non-encapsulated	Manganese Oxides	Carbonates	Iron Oxides
A	2.2	56.7	36.0	1.1	6.2
B	4.8	11.0	76.3	2.3	10.4
C	5.5	25.4	50.1	3.7	20.8
D	8.7	15.4	65.4	1.8	17.4
E	12.3	19.2	75.8	2.5	2.5

Silver minerals were not detected in the Ag-Mn ores by XRD because of their low content. To identify them, SEM was carried out on both the as-received samples and samples free of carbonates and Mn oxides. For the as-received samples, only very few Ag particles were detected. Silver was found finely incorporated in Mn oxides (Fig. 2). For the samples free of carbonates and Mn oxides, various Ag species were identified: silver (Ag), acanthite (Ag<sub>2</sub>S), cerargyrite (AgCl), embolite (Ag(Cl,Br)) and freibergite ((Ag,Fe,Zn,Cu)<sub>12</sub>Sb<sub>2</sub>S<sub>13</sub>). Figure 3 shows SEM photomicrographs of the various Ag minerals. Their size was less than 5 μm.

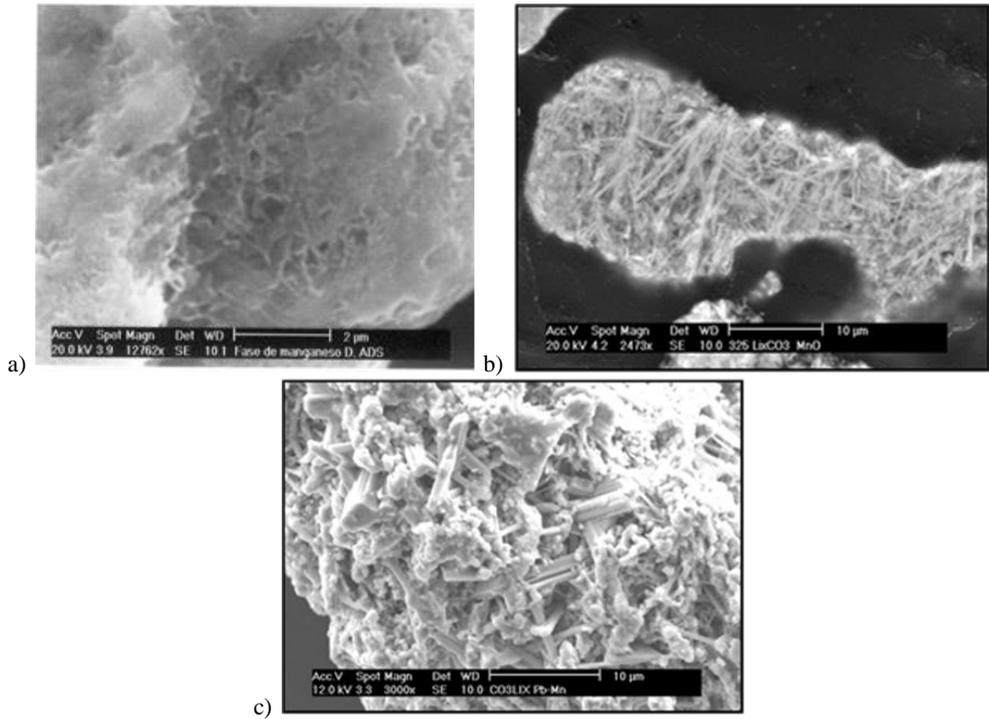


Fig. 1. SEM photomicrographs of manganese oxides in Ag-Mn ores from La Encantada mines: a) pyrolusite, b) johannsenite and d) quenselite

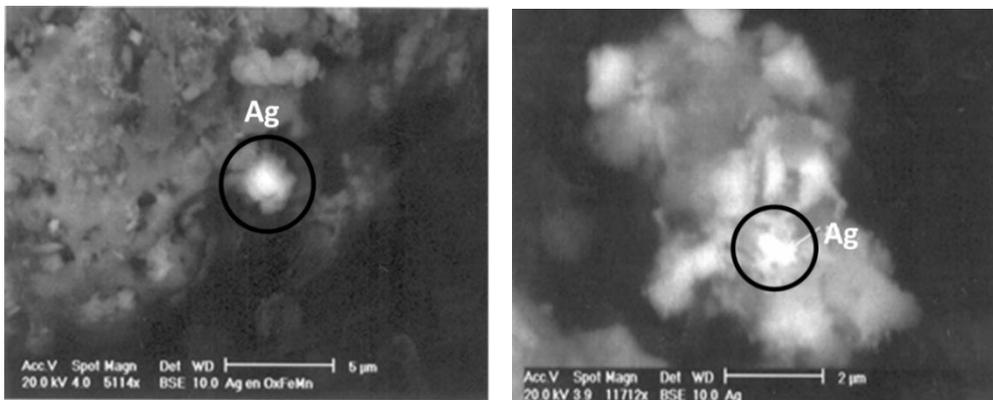


Fig. 2. Silver particles in manganese oxides

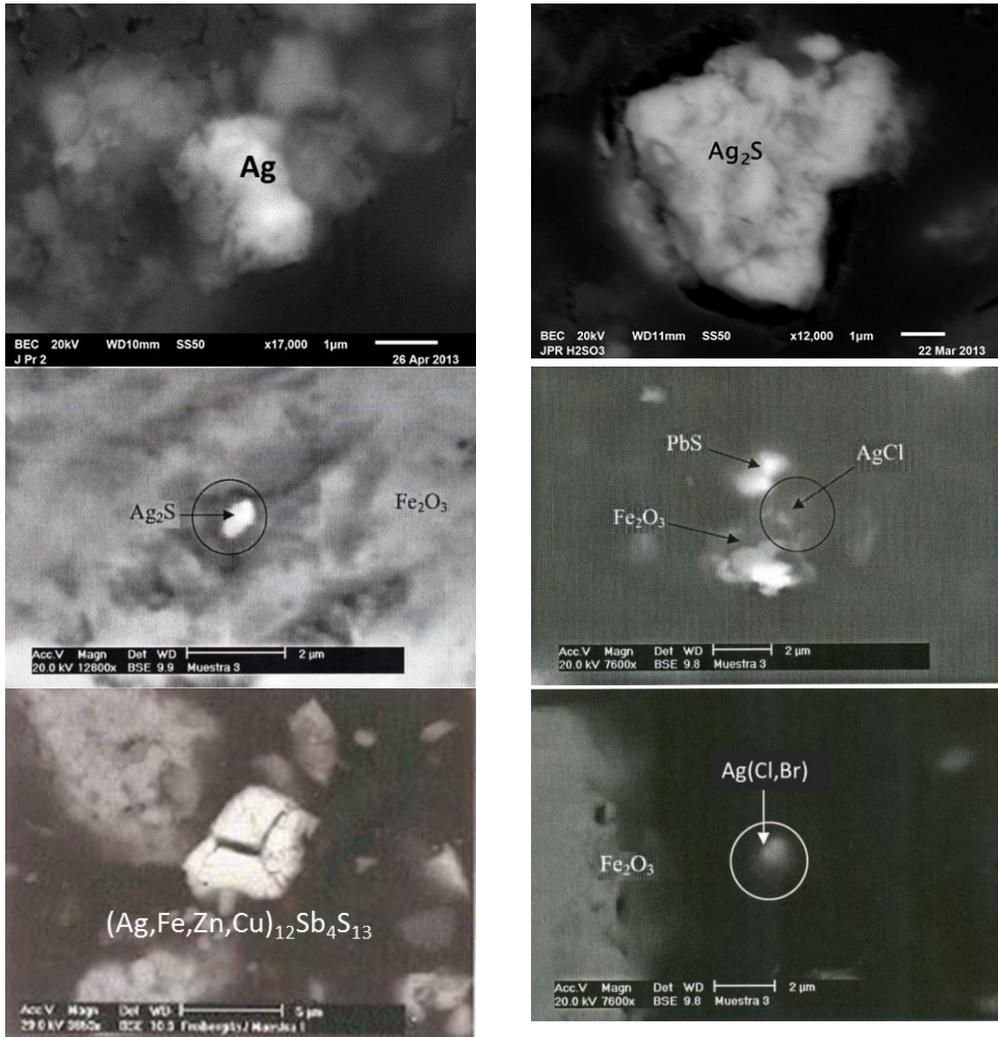


Fig. 3. Silver (Ag), acanthite (Ag<sub>2</sub>S), cerargyrite (AgCl), embolite (Ag(Cl,Br)), and freibergite ((Ag,Fe,Zn,Cu)<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>) in Ag-Mn samples free of calcite and manganese oxides

The low Ag recovery from Ag-Mn ores was commonly accounted for by the Ag being in the crystal lattice of Mn oxides (Siems, 1967; Hewett, 1968). To verify the presence of Ag in the crystal lattice of the pyrolusite, quenselite and johannsenite from the La Encantada ores, several particles of each of these minerals were examined by TEM. Figures 4a-c show the mineral electron diffraction patterns. These patterns were not affected by the possible presence of Ag since the experimental interplanar angles ( $\delta_{R1R2}$ ) determined from the electron diffraction are alike the calculated interplanar angles using the software Carine Version 3.0 (Table 3). As seen, the deviation between experimental and calculated interplanar angles is less than 2.3%.

Accordingly, Ag is not in the crystal lattice of the Mn oxide minerals. In addition, the TEM analyses revealed no Ag in the pores and inter-crystal spaces of the Mn oxides.

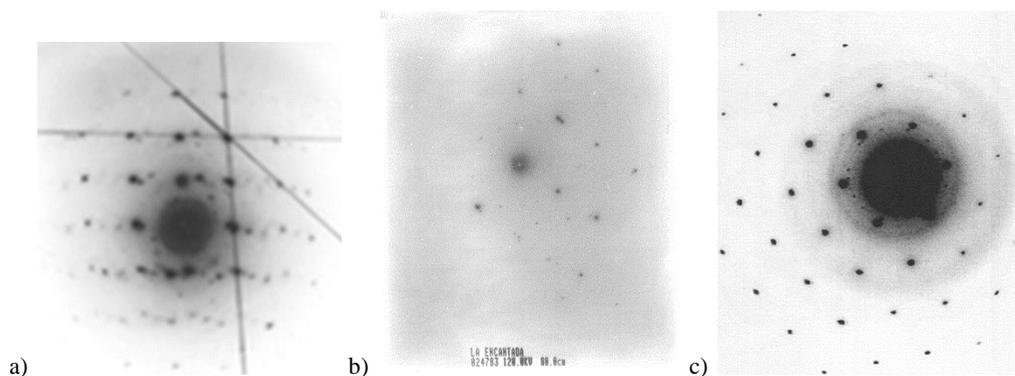


Fig. 4. TEM electron diffraction patterns for a) pyrolusite, b) quenselite and c) johannsenite

Table 3. Crystal structure, calculated and experimental interplanar angle for pyrolusite, johannsenite and quenselite

	Pyrolusite	Johannsenite	Quenselite	
Crystal Structure	Tetragonal	Monoclinic	Monoclinic	
Crystal planes	(1 1 -2) (2 0 -1)	(2 -1 0) (3 -2 -1)	(2 0 -3) (4 -2 0)	(1 -1 1) (2 0 1)
R1, cm	0.61	0.98	2.18	0.23
R2, cm	0.46	1.60	1.66	0.24
Calculated $\delta_{R1R2}$ angle	39.0	30.7	49.9	43.0
Experimental $\delta_{R1R2}$ angle	38.1	31.4	49.9	42.8
Deviation, %	2.3	2.3	0	0.5

Silver was not found in the crystal lattice of the Mn oxides. The low Ag recovery in cyanide leaching could be explained that Ag was encapsulated as very fine particles in the Mn oxides of the Ag-Mn ore. Additionally, during Ag cyanide leaching the samples were ground to an 80% passing size ( $K_{80}$ ) of 10  $\mu\text{m}$ . If Ag minerals were encapsulated in the Mn oxides, fine grinding would liberate them resulting in improvement of the Ag recovery. Figure 5 shows the Ag recovery by cyanide leaching as a function of particle size  $K_{80}$  for two of the Ag-Mn ore samples, that is the samples with the highest and lowest Mn grades. Decreasing the  $K_{80}$  value increased the Ag recovery. For the highest Mn grade sample, the recovery of silver increased from 13 to 26% when the sample was ground to  $K_{80}$  of 10  $\mu\text{m}$ , while for the lowest Mn grade sample the Ag recovery increased was from 56 to 62%. Likely, higher Ag recovery would be obtained where the samples were finer than 10  $\mu\text{m}$ .

Another evidence of Ag encapsulation in manganese oxides was the relationship between Ag recovery and the dissolution of Mn oxide. Controlled dissolution of Mn

oxide was effected with  $\text{SO}_2$ . Then, the  $\text{SO}_2$ -leach residue was subjected to cyanide leaching for the Ag recovery. As seen in Fig. 6, the Ag recovery proportionally increased with the dissolution of Mn oxide. The silver recovery higher than 90% was obtained upon complete dissolution of the Mn oxide. Unrecovered Ag can be accounted for by Ag encapsulated in the Fe oxides.

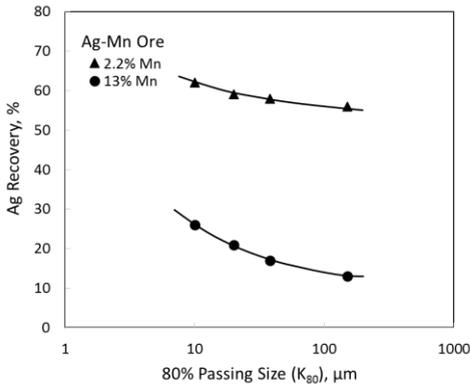


Fig. 5. Ag recovery by cyanide leaching as a function of 80% passing particle size

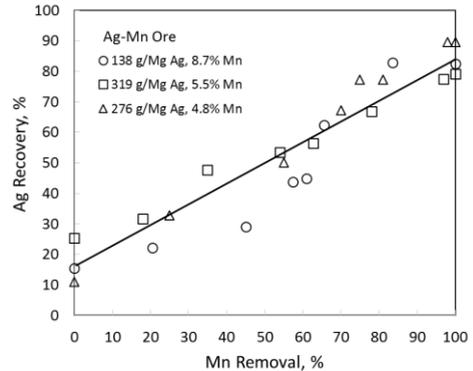


Fig. 6. Ag recovery in cyanide leaching as a function of manganese removal from Ag-Mn ore samples

## Conclusions

Silver in the Ag-Mn ore samples from La Encantada Mines in Mexico, was not found in the crystal lattice of the manganese oxides but as various minerals such as silver (Ag), acanthite ( $\text{Ag}_2\text{S}$ ), cerargyrite ( $\text{AgCl}$ ), embolite ( $\text{Ag}(\text{Cl},\text{Br})$ ) and freibergite ( $(\text{Ag},\text{Fe},\text{Zn},\text{Cu})_{12}\text{Sb}_2\text{S}_{13}$ ). These silver minerals were finely disseminated in iron oxides and mainly in the manganese oxides such as pyrolusite, quenselite and johannsenite. Silver recovery by cyanide leaching of the Ag-Mn ores was very low, but it was significantly improved by either fine grinding of the ores or dissolution of the manganese oxides prior to cyanide leaching.

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