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# USAGE OF REFRACTORY MATERIAL IN AN EARLY EASTERN ONTARIO LEAD SMELTER

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## ABSTRACT

A survey is presented regarding the practice of small-scale lead smelting in eastern Ontario during the first decade of this century. Refractory samples from the Hollandia lead mine (Ontario Mining and Smelting Company), near Bannockburn in the County of Hastings, were examined for alteration in mineral composition as a result of the smelting operation. Examination of the samples using electron-microprobe and optical microscope techniques suggests an operating temperature of approximately 1100°C in the smelter; as well, the fireclay refractory used was found to be chemically incompatible with the slag phase. The operation probably was abandoned primarily as a result of a change in owner, who favored a larger-capacity smelter located at a nearby rail-junction.

*Keywords:* refractory, lead smelter, eastern Ontario, historical.

## SOMMAIRE

On présente un aperçu des techniques d'extraction du plomb à petite échelle au tout début du siècle dans l'Est de l'Ontario. Des échantillons de brique réfractaire qui ont servi, à la mine Hollandia (alors propriété de la Ontario Mining and Smelting Company), près de Bannockburn, comté de Hastings, ont été examinés afin d'en évaluer les modifications en composition à la suite des opérations d'extraction. Les mesures à la microsonde électronique et les observations par microscopie optique montrent que la température a atteint 1100°C. Le matériau réfractaire s'est avéré chimiquement incompatible avec les scories. Le site aurait été abandonné surtout à cause d'un changement de propriétaire, qui favorisait un fourneau à plus grande capacité situé plus près d'une jonction ferroviaire.

(Traduit par la Rédaction)

*Mots-clés:* matériau réfractaire, fourneau d'extraction du plomb, région de l'Est de l'Ontario, historique.

## INTRODUCTION

At the turn of the century in eastern Ontario, there were several small lead mine–smelter operations producing quantities of pig lead in the order of 22–67 tonnes per year (OBM 1903, 1904a). Of these, one situated near Bannockburn, at the Hollandia lead mine, is of interest both because it is representative of a typical small-scale lead-mining operation in eastern Ontario, and because of the apparent misuse made of refractory material. For example, samples of refractory brick found at their original site by the authors in the spring of 1984 suggest that the type used (low-alumina fireclay) was ill-suited for the chemistry of the ore being smelted. The feed for this particular smelter consisted of hand-cobbed high-grade galena, averaging some 80% PbS, in a calcite gangue (OBM 1905a). Lead mining in eastern Ontario during the nineteenth and early twentieth centuries was almost totally confined to narrow, well-defined, nearly vertical fissure-veins filled with a gangue of calcite, minor barite and fluorite, and some quartz (Uglow 1916). The ore mineral was dominantly galena, with more or less sphalerite present in some veins. Anglesite, marcasite, pyrite, siderite and chalcopyrite are minor constituents of most veins (OBM, 1904b, Young 1909). These veins are distributed across eastern Ontario, western Quebec near Hull, and in northern New York State (Williams 1982). They are post-Ordovician in age, and are structurally related to Jurassic magmatism in the St. Lawrence Platform (Barnett *et al.* 1984). The veins cross-cut all types of country rock, ranging from Ordovician limestones and arkoses to Precambrian granites, marbles, gneisses, and diorites of Grenville age. Uglow (1916) gave detailed descriptions of most of the veins, as did Alcock (1930) and, more recently, Malczak *et al.* (1985).

The zoned or banded nature of the veins, taken together with the commonly coarse grain-size of the constituent minerals, meant that simple hand-mining methods ideally suited these orebodies. Subsequent hand-cobbing of the high-grade galena produced an acceptable smelter-feed.

In 1897 or 1898 the Hollandia mine was opened in Madoc Township, and was actively worked to 1904. By this time the operation was owned by the Ontario Mining and Smelting Company, which constructed a circular water-jacketed blast furnace (the subject of this study) at the site. In 1904, two carloads of pig lead were produced (OBM 1904c).

The smelter at the Hollandia mine was abandoned at the end of 1904, and a new smelter built at Bannockburn, some 5 km away (OBM 1905b).

Metallurgical practice at the time involved production of refractory materials from local clays where feasible; thus, the major chemical components of the product, which dictate the resulting refractoriness, namely alumina and silica, might vary considerably in concentration. The alumina content of the raw clay can vary from about 20 wt.% for residual clays and silts down to about 8 wt.% for marine and glacial clays (Twenhofel 1926, p. 186-197). Whereas a refractory clay consists essentially of kaolinite, the presence of fluxing oxides such as the alkalis and iron oxide result in a substantial lowering of the softening point of the refractory (Palfreyman 1973). Thus the refractoriness of a given brick used in early lead-smelting might well suffer from lack of compositional control, and vary considerably from brick to brick.

Lead-smelting practice *circa* 1900 did not always follow the roast–smelt sequence generally used today for sulfide ores. Rather, the ore was commonly first heated in air, offering a partial roast, followed by a further heating at an elevated temperature in the same furnace. This procedure produced some lead, and a "grey" slag, containing about 50% Pb, which was difficult to reduce further (Ingalls 1908) without using a shaft furnace. Although capital expenditures for such primitive furnaces were usually low, lead losses were correspondingly high, as the product generally consisted of pig lead, matte, slag, and partly reduced oxides. Also, fluxing practice was in its infancy, and whereas many slags were "self-fluxing", limestone and fluorspar additions were not generally made.

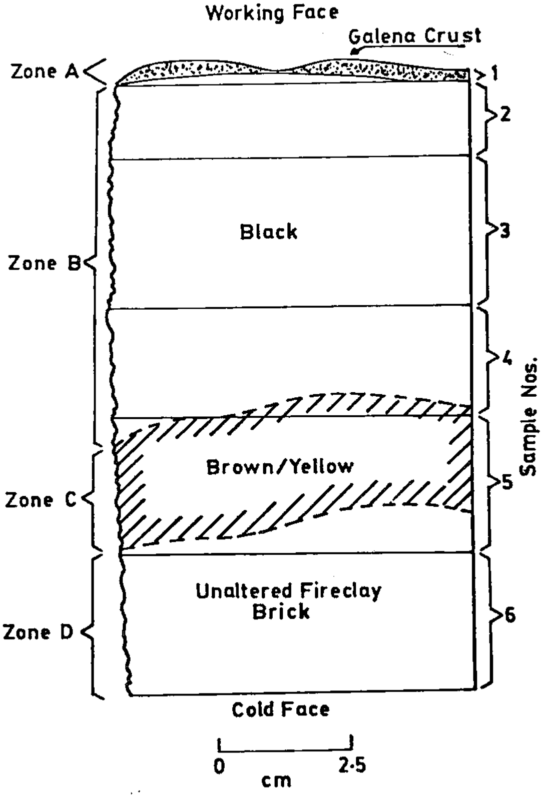

FIG. 1. Schematic diagram of section of refractory brick.

The roast–smelt sequence was uncomplicated by the need to recover silver since "silver values are very low, as would be expected in such low-temperature post-igneous veins" (Uglow 1916). Silver was only of economic interest where it exceeded 30 g/tonne, as it did in intermediate-temperature deposits (Uglow 1916).

The present paper explores the chemistry of the reactions related to smelting practice of the time, and contrasts this with present-day operations. In addition, reasons are suggested for the eventual abandonment of the mine–smelter operation.

## CHEMISTRY AND MINERALOGY

### *Chemistry*

Samples of brick from the circular water-jacketed blast furnace at the Hollandia lead mine were collected for examination and analysis by the authors in the spring of 1984. These samples are considered to be representative of material used for this purpose at Hollandia, and thus should reflect refractory usage and lead-smelting practice at the time.

In particular, one curved brick was chosen as being representative, and became the subject of this study. The brick displays a crust of galena (zone A) on the working face and three distinctively colored zones within the study brick itself; these zones are black, orange-yellow, and pale yellow, and labeled B, C, D, respectively (Fig. 1). The brick was cut into 6 rectangular blocks. The first (zone A) is the galena (matte) crust on the working face of the brick. The next three blocks were selected from the second or B zone (black); the fifth sample is from the orange-yellow C zone, whereas the sixth sample is from the unaltered pale yellow D zone away from the working face (Fig. 1). In addition, four polished sections were prepared; these represent the galena crust and the three colored zones (B, C, D). The sections were examined using optical and electron-microprobe techniques.

The six rectangular blocks were ground in a gyratory crusher. A 50-g sample was split from each original sample and further ground in an agate mortar to eliminate possible contamination by iron-group

TABLE 1. CHEMICAL COMPOSITION OF WHOLE-BRICK SAMPLES - OXIDES (1)

| Oxide (wt.%) | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
|---|---|---|---|---|---|
| $SiO_2$ | 51.7 | 52.6 | 53.9 | 57.3 | 57.9 |
| $Al_2O_3$ | 31.9 | 32.7 | 31.6 | 32.9 | 32.7 |
| CaO | 0.44 | 0.30 | 0.26 | 0.11 | 0.43 |
| MgO | 0.59 | 0.63 | 0.51 | 0.43 | 0.48 |
| $Na_2O$ | 0.50 | 0.45 | 0.34 | 0.14 | 0.17 |
| $K_2O$ | 0.95 | 0.91 | 1.01 | 1.24 | 1.25 |
| $Fe_2O_3$ | 7.27 | 4.84 | 6.91 | 4.70 | 4.41 |
| MnO | 0.02 | 0.02 | 0.03 | 0.04 | 0.04 |
| $TiO_2$ | 1.01 | 1.01 | 1.13 | 1.52 | 1.57 |
| $P_2O_5$ | 0.07 | 0.07 | 0.07 | 0.05 | 0.05 |
| Sum | 94.45 | 93.53 | 95.76 | 98.43 | 99.00 |
| LOI (2) | 5.55 | 6.47 | 4.24 | 1.57 | 1.00 |
| Total (3) | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

(1) Sample 1 not analyzed; all analyses by X-ray fluorescence spectrometry (X-ray Assay Laboratories, Toronto), detection limit 0.01%.

(2) LOI: Lost on ignition.

(3) Samples normalized to 100 wt.% for rock-forming elements analyzed as oxides.

TABLE 2. CHEMICAL COMPOSITION OF WHOLE-BRICK SAMPLES - ELEMENTS

| Element (1) | Analytical Method (2) | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 | Sample 6 |
|---|---|---|---|---|---|---|---|
| Pb | XRF | 81.2 | 24.9 | 26.1 | 15.9 | 1.25 | <0.01 |
| S | XRF | 8.72 | 3.39 | 3.86 | 2.37 | 0.15 | 0.03 |
| S(theor) | - | 12.69 | 3.85 | 4.03 | 2.46 | 0.19 | <0.01 |
| As | FAA | 22.0 | 6.9 | 5.2 | 3.2 | 2.0 | 0.4 |
| Sb | FAA | 4.8 | 5.7 | 7.8 | 11.0 | 2.5 | 1.0 |
| Ag | DCP | 3.0 | 2.5 | 3.0 | 5.4 | 1.5 | <0.5 |
| Co | DCP | 9 | 45 | 47 | 72 | 49 | 49 |
| Ni | DCP | 8 | 24 | 49 | 140 | 110 | 110 |
| Cu | DCP | 330 | 740 | 1100 | 1400 | 170 | 74 |
| Cr | XRF | - | 40 | 50 | 70 | 140 | 150 |
| Sr | XRF | <10 | 30 | 30 | 50 | 60 | 70 |
| Ba | XRF | 20 | 260 | 280 | 360 | 660 | 760 |
| Nb | XRF | <10 | 10 | 20 | 20 | 50 | 50 |
| Rb | XRF | 130 | 110 | 100 | 100 | 70 | 70 |
| Zr | XRF | 490 | 430 | 440 | 390 | 370 | 350 |
| V | DCP | 6 | 110 | 130 | 150 | 200 | 190 |
| Zn | DCP | 160 | 320 | 86 | 56 | 71 | 120 |

1 Pb and S, wt. %; other elements, ppm.
2 XRF X-ray fluorescence spectrometry, detection limit 10 ppm. DCP Direct-current argon-plasma emission spectrometry, detection limit 0.5 ppm (Ag, Cu, Zn), 1 ppm (Co, Ni), 2 ppm (V). FAA Flameless atomic absorption, detection limit 0.1 ppm. All analyses were carried out by X-Ray Assay Laboratories, Toronto, Ontario.

elements. Samples 1–6 were analyzed for 26 elements; results are presented in Table 1 (for oxides) and Table 2 (for elements).

### *Microscopy*

In addition to samples 1–6, described above, four sections were cut from a second similar refractory brick, cold-mounted, and polished using standard metallographic techniques. These sections are representative of the same four zones. Pertinent features and areas of interest were examined using an Olympus Model BHSP ore microscope. Qualitative microanalyses to assist in the identification of mineral phases were obtained using the electron-microprobe facilities in the Department of Geology, Queen's University, Kingston, Ontario.

## MINERALOGICAL ZONATION

The four polished sections display galena occurring as a massive 4-mm band on the working face (Fig. 2). Zone B (black) shows galena in small (0.1 - 0.01 mm) grains scattered throughout the matrix of the refractory brick (Fig. 3), making up between 20 and 30% of the section. The abundance of galena in Zone C is significantly reduced (approximately 1.5%, Fig. 4); it could not be detected at all in zone D.

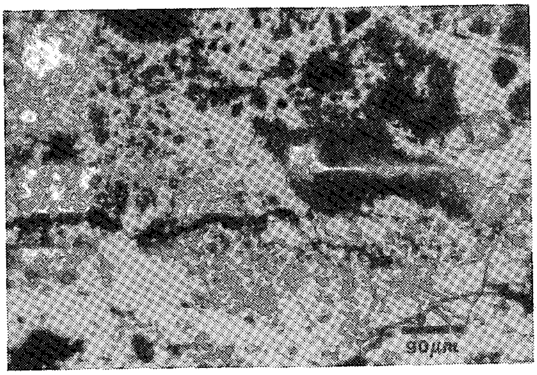

FIG. 2. The distribution of galena in Zone A. Galena is white; the aluminosilicate refractory is black.

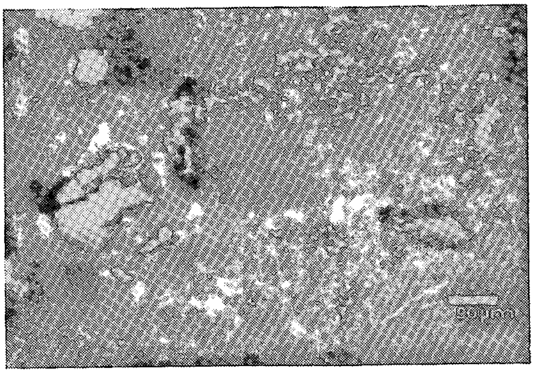

FIG. 3. The distribution of galena in Zone B. Galena (white) represents about 20% of the area; the remainder is the aluminosilicate refractory.

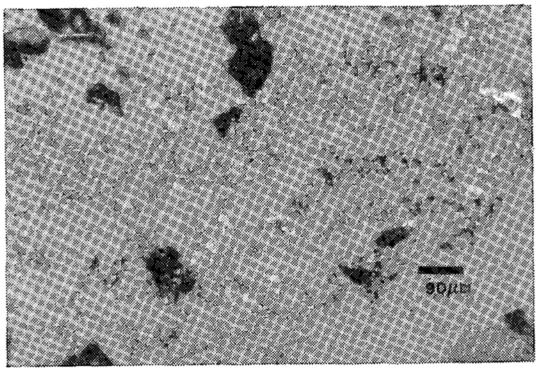

FIG. 4. The distribution of galena in Zone C. Galena (white) represents about 1.5% of the section; the remainder is the aluminosilicate refractory.

Minor quantities of pyrite were observed in the galena in zone B as tiny (0.01 - 0.03 mm) grains. They appear to have been exsolved from the galena, but the origin of the iron cannot be definitely attributed to either the ore or the refractory material.

Qualitative analyses by electron microprobe, using energy-dispersion spectrometry (EDS) were conducted on the four polished sections previously described, which represent the four visually distinct zones from the working face of the refractory to the cold face. Results of the microprobe work confirm the optical microscopy in every regard. Galena has penetrated the brick to a significant extent (at least 5 cm), grading from almost pure PbS at the working face to no PbS at the cold face. The grog grains (previously fired refractory material, crushed, and added to the clay to form the new brick), which are distributed homogeneously throughout the refractory, consist primarily of aluminosilicates with no PbS, and are poor in Ca, Ti and Fe. The fine-grained matrix (clay) has a higher incidence of alkalis, Ca, Ti and Fe, and PbS. Galena (the charge) represents about 90% of zone A. Zone B is black in color, a result of the fireclay refractory being pervasively invaded by fine-grained galena. Zone C has much less PbS relative to zone B, and grades from measureable PbS (dark) to trace PbS (pinkish yellow). Finally, zone D represents the refractory, relatively unaffected by its working environment.

## COMPOSITIONAL ZONATION

The chemical composition of the four zones (six samples) is given in Tables 1 and 2. The values for all samples in Table 1 have been normalized to 100%, as Pb and S were not included. Sample 6, which totalled 100.5 before normalization, contains no PbS (Table 2) and has been used as an indication of the original refractory chemistry (without PbS). This provides the justification for the normalization.

An examination of the compositions in Tables 1 and 2 shows that the elements fall into four distinct groups. The abundances of Pb, S, As, Rb, Zr and Na decrease away from the working face of the refractory, whereas Ba, Cr, V, Sr, Nb, K, Mn and Ti increase away from the working face. The elements Cu, Ni, Co, Ag and Sb show a maximum in the middle portion of the brick, and Si, Al, Mg and P are constant throughout the section. Ca, Fe and Zn show no consistent pattern of abundance from zone to zone.

These compositions reflect a combination of the effects of the thermal gradient from working face to cold face and the varying mobility of the various elements concerned. Those showing constant levels are components of the refractory itself, and are relatively immobile, as might be expected.

## DISCUSSION

Analytical data for zone A have shown that almost pure PbS was in a molten or semi-molten form at the working face of the refractory. This suggests that the ore was not completely preroasted and, in fact, the refractory bricks sampled were in contact with a matte phase. Furthermore, the matte consisted of essentially pure galena, which may react to form liquid, metallic lead and gaseous sulfur at 1107°C (Kubaschewski & Alcock 1979).

Whereas it is difficult to obtain a definite operating temperature from these assemblages, the fact that liquid PbS has permeated the refractory, as shown by the data in Table 2 and as illustrated schematically in Figure 1, suggests a temperature in excess of the melting point of galena, 1107°C. This temperature is also consistent with temperatures normally attained in other wood-fired furnaces such as pottery kilns (Rhodes 1971).

Recalling that standard present-day lead-smelting practice incorporates a roasting operation in which PbS is oxidized to PbO at approximately 900°C, the retention of PbS suggests that on the first firing, liquid PbS permeated the working face before freezing. This would initially protect the refractory (chemically acidic) from the slag (chemically basic). Additional information obtained from Table 2 indicates that lead in a form other than a sulfide (PbO, $PbSO_4$, or both) was also present at the working face, and probably in the molten or semimolten charge itself.

Historical fact shows that this lead smelter was used briefly in 1904 to produce only 47 tonnes of pig lead (OBM 1904a). This would have been accomplished in a few heats, no doubt for a total operating duration of several days. It is probable that thermal equilibrium could be reached in a few hours, but quite unlikely that the element distribution observed in the refractory represents chemical equilibrium between the molten PbS charge and the cold face. Rather, it is a "frozen" picture of a dynamic system of mobile elements. Indeed, the rapid and deep penetration of the brick by elements from the charge (*e.g.*, Pb, Cu) suggests that chemical equilibrium could never be achieved; instead, rapid breakdown of the refractory as a result of slag–refractory incompatibility would be the expected outcome of repeated use of the smelter.

Because of this chemical nonequilibrium, little can be concluded from those elements whose abundances either increase or decrease steadily away from the working face. However, the case is different for those elements attaining maxima in the middle portion of the brick. Their maxima may represent the formation of mineral assemblages presumed to be stable at the working temperature reached in the brick at the loci of the maxima, which are spatially coincident. These loci are a function of the rapid thermal attenuation away from the working face as well as the relatively similar mobility of the elements concerned.

Table 2 shows that Sb, Ag, Co, Ni and Cu concentrate near the centre of the refractory. The occurrence of Ag with Sb and Cu is well documented in lead refining (Dugdale & Young 1975), where these elements must be removed as a sulfide (in the case of Cu) or by selective oxidation (in the case of $Sb_2O_3$), before the Ag may be separated from the Pb. The suggestion is that these elements have permeated the refractory along with the galena in the original ore, and have deposited at a location in the brick where the temperature has lowered below their crystallization point.

With regard to additions of flux, there is no evidence of their deliberate use either historically or chemically at the Hollandia smelter, although subsequent operations at Bannockburn, at the smelter of the Stanley Smelting Company (OBM 1905c), relied on materials such as silica and hematite to fluidize their slags. Part of the reason for the non-use of flux at the Hollandia smelter might have been the calcite gangue (which also contains traces of fluorite); this assemblage could have provided a "self-fluxing" slag.

An additional consideration when comparing the Hollandia smelter to present lead-smelting practice lies in the choice of refractory. Whereas fireclay refractories were commonly used at the turn of the century, more recent refractory practice suggests the use of basic brick for ore of this chemistry. Of particular note are the magnesite, chrome–magnesite, and magnesite–chrome refractories, which have replaced fireclay, not only in lead smelting, but also for specialized operations in steelmaking, such as the lining of desulfurizing ladles. Thus, it is suggested that the refractory used at Hollandia could not have withstood the rigors of present-day lead smelting.

## SUMMARY AND CONCLUSIONS

1. A chemical outline has been given of a small-scale, turn-of-the-century lead mine and smelter in eastern Ontario.
2. It has been shown that the chemistry of the ore was not compatible with the type of refractory used, and that the matte permeated one third to one half of the brick. However, the lining still survived this particular operation. This was probably a result of a relatively low residence-time of the melt in the shaft furnace, and initial "protection" of the working face by galena, combined with the small number of heats to which the refractory was exposed.
3. The smelter at Hollandia was most likely abandoned because it did not suit the plans of the Stanley Smelting Company, which took over from the Ontario Smelting and Refining Company in 1905. The Stanley Smelting Company wanted a smelter with a much larger capacity, and located at a nearby rail-junction, thus capable of drawing on several mines for ore.

## ACKNOWLEDGEMENTS

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