

with the formula  $\text{PbSiF}_6 \cdot 4\text{H}_2\text{O}$ . This salt dissolves at 15 degrees C. in 28 per cent. of its weight of water, making a syrupy solution of 2.38 sp. gr. Heated to 60 degree C., it melts in its water of crystallization. A neutral solution of lead-fluosilicate is partially decomposed on heating, with the formation of a basic insoluble salt and free fluosilic acid, which keeps the rest of the salt in solution. This decomposition ends when the solution contains, perhaps, 2 per cent. of free acid; and the solution may then be evaporated without further decomposition. The solutions desired for refining are not liable to this decomposition, since they contain much more than 2 per cent. of free acid. The electrical conductivity depends mainly on the acidity of the solution.

My first experiments were carried out without the addition of gelatine to the fluosilicate solution. The lead-deposit consisted of more or less separate crystals that grew toward the anodes, and, finally, caused short circuits. The cathodes, which were sheet-iron plates, lead-plated and paraffined, had to be removed periodically from the tanks and passed through rolls, to pack down the lead. When gelatine has been added in small quantities, the density of the lead is greater than can be produced by rolling the crystalline deposit, unless great pressure is used.

The Canadian Smelting Works, Trail, British Columbia, have installed a refinery, making use of this process. There are 28 refining tanks, each 86 in. long, 30 in. wide and 42 in. deep, and each receiving 22 anodes of lead-bullion with an area of 26 by 33 in. exposed to the electrolyte on each side, and 23 cathodes of sheet-lead, about 1-16 in. thick, prepared by deposition on lead-plated and paraffined-iron cathodes. The cathodes are suspended from 0.5 by 1 in. copper bars, resting crosswise on the sides of the tanks. The experiment has been thoroughly tried, of using iron sheets to receive a deposit thicker than 1-16 in.; that is, suitable for direct melting without the necessity of increasing its weight by further deposition as an independent cathode; but the iron sheets are expensive, and are slowly pitted by the action of the acid solution; and the lead deposits thus obtained are much less smooth and pure than those on lead sheets.

The smoothness and the purity of the deposited lead are proportional. Most of the impurity seems to be introduced mechanically through the attachment of floating particles of slime to irregularities on the cathodes. The effect of roughness is cumulative; it is often observed that particles of slime attract an undue amount of current, resulting in the lumps seen on the cathodes. Samples taken at the same time showed from 1 to 2.5 oz. silver per ton in rough pieces from the iron cathodes, 0.25 oz. as an average for the lead sheet cathodes and only 0.04 oz. in samples selected for their smoothness. The variation in the amount of silver (which is determined frequently) in the samples of refined lead is attributed not to the greater or less turbidity of the electrolyte at different times, but to the employment of new men in the refinery, who require some experience before they remove cath-

odes without detaching some slime from the neighbouring anodes.

The shape of the electrodes, and the method of handling them to and from the tanks, are shown in Fig. 1.

Each tank is capable of yielding, with a current of 4000 amperes, 750 lbs. of refined lead per day. The voltage required to pass this current was higher than expected, as explained below; and for this reason, and also because the losses of solution were very heavy until proper apparatus was put in to wash thoroughly the large volume of slime produced (resulting in a weakened electrolyte), the current used has probably averaged 3000 amperes. The short circuits were also troublesome, though this difficulty has been greatly reduced by frequent inspection and careful placing of the electrodes. At one time, the solution in use had the following composition in grammes per 100 c.c.: Pb, 6.07; Sb, 0.0192; Fe, 0.2490;  $\text{SiF}_6$ , 6.93, and As, a trace. The current passing was 2800 amperes, with an average of about 0.44 volts per tank, including bus-bars and contacts. It is not known what was the loss of efficiency on that date, due to short circuits; and it is, therefore, impossible to say what resistance this electrolyte constituted.

Hydrofluoric acid of 35 per cent. used as a starting material for the preparation of the electrolyte is run by gravity through a series of tanks for conversion into lead fluosilicate. In the top tank is a layer of quartz 2 feet thick, in passing through which the hydrofluoric acid dissolves silica, forming fluosilicic acid. White lead (lead carbonate) in the required quantity is added in the next tank, where it dissolves readily and completely with effervescence. All sulphuric acid and any hydrofluoric acid that may not have reacted with silica settle out in combination with lead as lead sulphate and lead fluoride. Lead fluosilicate is one of the most soluble of salts; so there is never any danger of its crystallizing out at any degree of concentration possible under this method. The lead solution is then filtered and run by gravity into the refining tanks.

The solution originally used at Trail contained about 6 per cent. Pb and 15 per cent.  $\text{SiF}_6$ .

The electrical resistance in the tanks was found to be greater than had been calculated for the same solution, plus an allowance for loss of voltage in the contacts and conductors. This is partly, at least, due to the resistance to free motion of the electrolyte, in the neighbourhood of the anode, offered by a layer of slime which may be anything up to half an inch thick. During electrolysis, the  $\text{SiF}_6$  ions travel toward the anodes, and there combine with lead. The lead and hydrogen travel in the opposite direction and out of the slime; but there are comparatively few lead ions present, so that the solution in the neighbourhood of the anodes must increase in concentration and tend to become neutral. This greater concentration causes an E. M. F. of polarization to act against the E. M. F. of the dynamo. This amounted to about 0.02 v. for each tank. The greater effect comes from the greater resistance of the neutral solution with which the slime is saturated. There is, consequently, an ad-