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D00065

**ID**

United Nations Industrial Development Organization

Distribution  
LIMITED

ID/WG.33/3  
24 February 1969

ORIGINAL: ENGLISH

Expert Group Meeting on Lead and Zinc Production  
London, England, 28 April - 2 May 1969

ELECTROLYTIC LEAD REFINING <sup>1/</sup>

by

E. R. Freni  
Monteponi & Montecatini S.P.A.  
Italy

<sup>1/</sup> The views and opinions expressed in this paper are those of the author and do not necessarily reflect the views of the secretariat of UNIDO. The document is presented as submitted by the author, without re-editing.

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ELECTROLYTIC LEAD REFINING

by Dr. Elie P. Freni  
of

MONTEPONI & MONTEVECCHIO S.P.A.  
Via Vittor Pisani n. 19  
Milano (Italia)

Summary

A very large number of electrolytes have been studied and suggested for lead electrolytic refining, but it was Anson G. Betts who came up with a really practical solution of the problem by developing industrial application of the electrolyte based on lead fluosilicate. The first electrolytic refining plant built according to Betts' process, that of the Consolidated Smelting and Refining Co., of Trail, in Canada, has been in continuous operation since 1903. At present there are about ten plants for electrolytic lead refining scattered throughout the world. Here in particular, we are illustrating the characteristics and technological and economic results of the San Gavino plant in Sardinia, operated by Monteponi & Montevecchio. This plant started production in 1957, initially using an electrolyte based on lead sulphamate. Subsequently, the sulphamate electrolyte was gradually and progressively changed into fluosilicate electrolyte. A peculiar characteristic of this plant is the high degree of automation which has permitted to restrict operating costs to extremely convenient limits. Its productive capacity is 105 metric tons of refined lead daily, and it has replaced a thermic plant which had operated for 25 years according to the classic Parkes' process. The lead to be treated, which contains large percentages of Ag, Bi, Cu, Sb and As, is skimmed and cast into anodes, by means of a completely automatic plant which supplies racks of anodes ready for introduction into the cells. The starting cathodes consist of thin sheets of lead which are also produced by means of a special automatic machine. The cathodes are extracted in complete racks from the cells, re-melted, and automatically cast into ingots. Power density for the operation varies from 140 to 210 A/mg. according to the impurity content of the anodes, with a power efficiency of about 9%. Refined lead containing: Sb = 0,0001 - 0,000% ; As = 0,0001% ; Cu = 0,0003 - 0,0007% ; Bi = 0,0001 - 0,0004% ; Ag = 0,0001 - 0,0004%. is obtained from anodes containing Sb = 1,5-2,5% ; As = 0,2-0,5% ; Cu = 0,02 - 0,04% ; Bi = 0,1-0,3% ; Ag = 0,1 - 1%.

With progressive dissolving of the anodes, the impurities associated with the lead form a compact spongy layer of sludge which, when subsequently treated, yields all the constituent metals. Treatment of the sludge is based on progressive oxidation of the more easily oxidized elements according to a sequence of reducing and oxidizing melting operations which permits final separation of the noble metals in the form of oxides. These operations are performed in a rotary furnace, a converter and a Cupel furnace. The copper dross obtained from skimming of bullion are processed in rotary furnaces to recover the lead which is returned to the refining cycle, while the copper is recovered in the form of matte and speiss. The electrolytic process permits refining of impure lead in a single stage, with marked lesser production of intermediate recycling by-products typical of heat processes. Large amounts of impurities are tolerated in the lead to be refined, while the purity of the refined metal remains consistently above 99.995%. When refining of bismuth and subsequent recovery of this metal is to be performed, the electrolytic method especially reveals its efficiency, elasticity and convenience. Another characteristic of the electrolytic process is the hygienic nature of the work premises.

On July 1, 1968, a plant for electrolytic lead refining started operating at Copșa Nica, in Romania; it was planned and built by Monteponi & Montevocchio on behalf of the Roumanian Government. This plant has an annual capacity of 40.000 metric tons of refined lead and processes the impure lead produced by the locally installed ISP. In planning and building this plant, which has immediately reached most outstanding running performances, all the experiences and results of refining at San Gavino have been condensed, thus obtaining a further great cut in consumption and operating costs.

Other plants, of up to 60.000 metric tons capacity yearly, are now in the planning stage, and the application of increasingly sophisticated techniques permits to envisage economic and technological results of extremely satisfactory nature, superior to those of any other alternative process.

Dr. Elie Freni

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by Dr. Elio R. Freni

of

MONTEPONI & MONTEVECCHIO S.P.A.

Via Vittor Pisani n. 19

Milano (Italia)

Introduction

1. A large number of electrolytes has been studied and proposed for electro-deposition of lead. First trials were carried out by Hampe with an acetate electrolyte. His experimental works were continued and developed by Keit who tried to set up the refining of lead on industrial scale, using as electrolyte a solution of lead sulphate in lead acetate. The process was employed by an american plant and a refined lead with 99.99 % Pb was obtained from anodes with a lead content of 96-97 %. This process was then discontinued due to the high operational costs as well as to low convenience, as the cathodic deposit was made of thin and dispersed metallic sponge.
2. Anson G. Betts gave a practical solution to the problem of electrolytic refining of lead. The researches of Betts covered the field of a large number of complex acids: fluosilicic, fluoboric, ditionic, metil and etil sulphoric and many sulphonic acids, giving high solubility lead salts and high conductivity solutions. He found that adding an organical colloid, as glue or gelatine, to one of these electrolytes, leads to the forming of a solid, compact and adherent cathodic deposit, showing the same density of the metal in ingots. Due to operating costs, the flusilicic electrolyte has been preferred for lead refining, besides fluoborates and sulphonates have put few applications in plating.
3. The fist electrolytic refining plant, using the Betts process, owned by the Consolidated Smelting Refining Co. in Trail - Canada is running continuously since 1903, after several enlargements and renewals until the present max. capacity of 600 tons per day. The plant of U.S. Smelting Lead Refinery Inc. at East Chicago started the production in 1906 and it has been largely renewed during the last years to the present capacity of 40.000 tone per year. The plant of Cerro de Pasco Copper Corp. at Oroya, Peru, built in 1934 and enlarged in 1937 was designed aiming to refine a typical low grade bullion and for the

max capacity of 80.000 tons per year of refined lead. Other electrolytic lead plants are in Paderno Dugnano - Italy, using sulphamic electrolyte; in San Gavino Monreale - Italy, in Freiberg - DDR, in Befe - Japan. The plant of Coppa Mica - Rumania has been the last one to start production in July 1968.

The plant in question with a capacity of 40,000 tons per year was designed and built by Monteponi & Montevecchio on behalf of the Rumanian Government.

4. Several inventors suggested, after Betts, various different electrolytes: oxalates, lactates, cyanites, nitrates, perchlorates, plumbates, formamides, ammonia, etc. In practice, only five electrolytes gave good results: fluoboric, fluosilicic, phenol sulphonic, perchloric, sulphamic. Small quantities of organic "agents" are added to have good deposits which are not different each other when the thickness is less than 0,2 - 0,3 mm., whilst appreciable differences arise with thicker deposits. In case of refining, the economical convenience to get cathodic deposits as thicker as possible, limits the choice to fluosilicates and fluoborates. The latter, as mentioned above, are avoided because of their high cost.

5. It must be so stated that every new electrolyte to be used for lead refining must be evaluated and compared along with the fluosilicic electrolyte.

#### Lead Electrolysis in San Gavino

6. The San Gavino Smelter of Monteponi & Montevecchio Co., situated 50 km. North of Cagliari in Sardinia, was built in 1932 for the treatment of the lead ores produced 20 km. distant in the Montevecchio Mine. The original capacity of the plant was 12,000 tons per year of lead thermally refined by Parkes process. The bullion was produced by a circular blast furnace of 1.20 m. diameter. In 1938 the potentiality of the blast was brought up to 36,000 tons per year with the installation of a rectangular blast furnace having a 120 tons/day output of lead bullion, and the enlargement of the thermal refining plant. For the entire war period and up to 1946-47 the plant treated almost exclusively the ores of Montevecchio, from which was obtained a bullion of constant composition similar to the following: Sb 0,3% - Cu 0,2% - As 0,1% - Ag 0,075% - Bi 0,0020%.

7. Later, as stoping decreased in the Montevecchio Mine there was a progressive rise in the bismuth percentage in the galena. At the same time, the purchase of custom concentrates and the treatment of the toll ores (on behalf of

third parties) determined such an increase of the new impurity that it was necessary to institute a new process capable of eliminating the bismuth from the lead.

8. In those years a new electrolyte using sulphamic acid was developed. The use of electrolytes with sulphamic acid salts was introduced into hydrometallurgy and electroplating by L. Cambi and R. Piontelli who used them in 1937 and who in 1938 patented the use of sulphamic acid as an electrolyte for metallurgical applications. In 1948 a plant with a capacity of 10 tons per day, and using sulphamic acid was started in Paderno Dugnano (Milano) from the Tonolli Co.

9. Sulphamic acid is a strong acid (sometimes called solid sulphoric acid) with the formula  $\text{HNH}_2\text{SO}_3$ , non hygroscopic, non poisonous. Its salts have elevated solubility, a fundamental prerequisite for use, and almost all of them offer high chemical stability. In the case of electrolytic lead refining, from an examination of the polarization curves for the various metals in 0,5M solution, it results that:

1) the most important and insidious impurities as Bi, As, Sb and Ag are practically insoluble; 2) The tin forms an unstable salt; 3) While the copper polarization is very high, the polarization of both cathodic and anodic lead is very low. All these properties put sulphamic electrolyte on the same level as fluosilicic electrolyte as far as selective capacity is concerned. But the facility in preparing sulphamic acid, its physical characteristics of ease in handling and in transport, and its availability on the Italian market while the probability of obtaining hydrofluosilicic acid was nil in Sardinia called the attention of the Montecatini firm to its possibilities in production.

#### Research and Pilot Testing

10. First research on the use of sulphamic acid as electrolyte for lead refining was begun in 1948 by the research department of the factory. The purpose of the research was to determine the composition of the electrolyte and the type and quantity of "addition agents" to send in solution periodically to obtain thick and compact cathode deposits. The problem of obtaining good cathode deposits in the electrolysis of lead salts lies, as is well known, in finding such "addition agents" that, absorbing themselves on the metal during electrolysis, diminish the grain and inhibit its growth in certain directions, principally along the lines of force of the electric field. The research



program then considered studying the possibilities of using the new electrolyte in confronting the maximum content of tolerable impurities in the anodes and the definition of the technical particulars and details for the realization of an economical industrial cycle.

11. In the tests at San Gavino the entire range of concentrations of sulphamic acid and lead sulphamate was examined from 5 to 100 gr/liter of free acid and from 100 to 300 gr/liter of lead sulphamate corresponding to 50 - 150 gr/liter of Pb with a current density of 100 A/sq.m. under a voltage varying from 0,5 to 0,7 volts per cell. A total concentration of free acid plus combined acid plus lead of 250 - 300 gr/l. corresponded to the lower voltage. Inside this field the concentrations vary amply without bringing appreciable variations in conductivity.

12. To determine the organic additives, numerous substances were examined and the choice went to two of them - glue and bindarene ( a sulphitic extract of wood resulting from the bisulphitic treatment for cellulose) which, added to the electrolyte at 2 - 3 gr/liter, allowed the formation of compact cathodic deposits. Later, a third additive was introduced - phenol, which gave brilliant results. The tests described, conducted in a small, 3 cell pilot plant led, in 1952, to the starting of a first pilot plant with a 3,5 ton/day capacity.

#### Pilot Plant and Semi-industrial Plant

13. This plant, composed of 36 cells, had the immediate purpose of electrolytically refining about 1000 tons per year of lead especially impure for a high content of Sb, As, and Bi. However, the most important object was the observation of the various consumptions and the checking of the electrolyte over a period of time.

14. The electrolyte (prepared by dissolving litharge in a solution of sulphamic acid by mechanical agitation) was composed of: free  $\text{H}_2\text{SO}_3$  - 80 gr/liter;  $\text{Pb}(\text{NH}_2\text{SO}_3)_2$  - 160 gr/l; Pb - 80 gr/l.; Bindarene - 2+4 gr/l.; glue - 2 gr/l. Phenol - 4 gr/l.

15. In every cell, built in reinforced concrete lined with P.V.C. and with the dimensions of 75 x 225 x 110 cm., there were 20 cathodes of stainless steel 18 - 8 and 21 anodes weighing 100 Kgs. each with the following average composition: Sb = 1,5 - 2% ; As = 0,2 - 0,3% ; Cu = 0,05% - Bi = 0,01 - 0,3% ; Ag = 0,1 - 0,3% ; Pb = 95 - 97 %.

16. With a current density of 100 A/sq.m., in two years electrolytic lead of the following purities was produced: Sb = 0,0005 - 0,0010% ; As = absent ; Cu = 0,005 - 0,0010% ; Bi = 0,0003% ; Ag = 0,0001% ; Pb = 99,995 - 99,998 % ; The current efficiency was about 95% and the cathode deposits on stainless steel reached compact thicknesses of 7+8 mm. on each face of the cathode in a six-day immersion period.

17. In two full years of operation there was the following consumption per ton of refined lead: Sulphamic acid = 2,8 Kgs. ; Litharge = 2 kgs. ; Bindarene = 0,8 kgs. ; Phenol = 0,7 kgs. ; Glue = 0,4 kgs. ; Power (DC) = 190 kwh.

18. After these results and a fine tuning of the process for recovering the metals in the anode slime (Ag, Bi, Sb, Pb, Cu), it was decided to enlarge the pilot plant to a semi-industrial plant with a 15 ton/day production. This plant, installed in the same room that had held the first pilot plant, went into operation early in 1955. In two years' activity the results obtained previously were confirmed and improved upon.

19; The action of the surface-active substances in the chrystalization process of the metal that deposits on the cathodes is explained in different ways but the solution of the problem was found only after successive practical tests which required prolonged periods of tests and statistical surveys to determine the accumulating action which hardly ever takes place in the small-scale tests because the volumes in play are exceptionally influenced by the renewal of the electrolytic solutions added to compensate for loss, even mechanical.

20. The addition of phenol, glue and bindarene together permitted the continuation for long periods of time of results of great practical importance: 1) The avoidance of the formation of spungy or incoherent deposits. 2) Of having decisively plastic deposits, suseptible of being bent and stretched with the same ease as a rolled section, a very important characteristic for cathode starting sheet production from steel cathode deposits. 3) Of increasing cathode deposit thickness with a consequent increase in the cathode immersion time.

21. The difficulties in analytically controlling the maintenance of addition agent concentration in the electrolyte caused practical inconveniences at one time that manifested themselves above all by an excessive formation of foam , incrustations of solid, mucilaginous, and gummy substances in the pipes, canals, and circulation pumps of the electrolyte.

22. Of the three additives, only phenol was analytically determinable. For the glue and bindarene the only reference was the aspect of the deposit and the data consequently inferred from practice, which established the consumption per ton of refined lead: Phenol = 0,7 kgs. ; Glue = 0,4 kgs. ; Bindarene = 0,8 kgs.

23. Furthermore, it was not improbable to suppose that the oxidation products of the glue and bindarene that accumulated in the electrolyte had a harmful effect since in fact it was sometimes seen that the cathode deposits suddenly worsened, whether the daily addition was continued (in which case spungy rather than compact deposits were obtained) or not (in which case needlelike and fragile deposits were obtained). These inconveniences assumed relevant importance only in the semi-industrial plant and caused a re-examination of the addition agent problem, extending the tests to a series of products even vaster than that at the beginning.

24. The first thing to come to light was the possibility of substituting saccharose for glue, eliminating the formation of the gummy substances and introducing a second easily analytically assayable product into the electrolyte.

25. Later on the point was reached where excellent results were obtained using just one addition agent of easy and rapid analytical determination - tannin (tannic acid) at a rate of 1 - 2 gr/liter, with a consumption of only 200 grams per ton of refined lead.

26. On the basis of these results, the optimum conditions for the sulphamic electrolyte resulted as a solution containing: 80 - 85 gr/lt. of Pb ; 45 - 50 gr/lt. of free  $\text{NH}_2\text{HSO}_3$  ; and 1 - 2 gr/lt. of tannin. In five years of operation it was never necessary to renew the electrolyte because of an accumulation of impurities. Their percentages never exceeded the following: Cu = 0,001 gr/lt. ; As = 0,005 gr/lt. ; Fe = 0,28 gr/lt. ; Ni = 0,008 gr/lt. ; Sb = 0,1 gr/lt. ; Zn = 0,22 gr/lt. ; Ca = 2,1 gr/lt. ; Cl = 0,4 gr/lt.

In practice, only periodic additions of sulphamic acid (to maintain at a constant level both the free acidity and the total volume of the electrolyte) and of lead sulphamate (to compensate for mechanical losses) were necessary.

27. During the entire pilot production period about 14.000 tons of bullion were refined and the extremely high selective power of the sulphamic electrolyte, especially as regards Ag, Sb and Bi, was noted.

28. For about two years, in some cells of the plant, even anodes of "rich lead" having 8-9% of Ag ; 0,3-0,5% of Cu were refined with continuity, thus obtaining electrolytic lead having 0,0003 - 0,0004% Ag and 0,0010 - 0,0015% Cu.

29. As for bismuth, with a percentage of Bi in the anodes of about 0,08%, the percentage in the refined lead was never above 0,0001%. In several periods of some months each, only anodes with a percentage of Bi between 0,2 and 0,4 were subjected to refining. In these cases the percentage of Bi in the refined lead was always about 0,0003 - 0,0004%.

30. The results obtained in the two plants permitted a direct comparison of costs between the new electrolytic process and the classic thermal refining method, both used in the San Gavino Plant. Where the ores contained no bismuth, the costs were equal. But when the ores contained a high percentage of bismuth, there was a saving of about 20% with the electrolytic process. This refers to the intrinsic cost of refining alone.

#### Choice

31. Keeping in mind that a metallurgic establishment can only very rarely be designed for handling only one constant type of ore, the possibility of receiving and treating ores from many different sources means higher productivity and lower production cost. But the receptivity of a plant is bound to its elasticity and universality of treatment.

32. In San Gavino the average percentage of Bi in the concentrates rose gradually and continuously, in the ten years from 1946 to 1956, from 0,0020 - 0,0030 to 0,06 - 0,09. The processing of lead to the impurity percentage fixed by the Italian market would require either cutting the annual production in half by rejecting the bismuthiferous ores, or a complicated and arduous job of subdividing and reserving for special thermal treatment the bismuthiferous and non-bismuthiferous ores; or the adoption of the Kroll-Betterton process for refining the bismuthiferous lead produced; or the adoption of electrolytic refining.

Let's examine the four cases:

33. 1) The rejection of the bismuthiferous ores would mean cutting production in half. The disadvantages of such a solution are quite obvious.

34. 2) The separate treatment (smelting and refining) of the bismuthiferous and non-bismuthiferous ores would mean subdividing the working cycle of the plant into two parallel working cycles, each one reduced, bringing an increase in

the production costs of not less than 50%. And the marketable metal would meet only a part of the market requirements.

35. 3) The adoption of the Kroll-Betterton process would cause an increase of not less than 20% on the cost price without bringing corresponding advantages.

36. 4) The adoption of the electrolytic process would give ample elasticity; the possibility of accepting any type of ore with any percentage of any type of impurity; a very high refined metal strength in every case; a cost price equal or inferior to that obtained by thermal refining of lead not containing bismuth. These results led Montevecchio to the conversion of its refining from thermal to electrolytic refining.

#### Sulphamic electrolyte plant.

37. The new electrolytic refining plant (fig. 1), designed for sulphamic electrolyte use with a current density of 100 A/sq.m., has a maximum productive capacity of 100 tons/day with a current density of 140 A/sq.m. Its productive activity started at the beginning of 1957. The experiences and observations made on the pilot plants were used in the design. A very high level of mechanization and automation permits such a small labor force that cost of production is much lower than with thermal lead, independently from bismuth purification.

#### Bullion Dressing

38. Equipment for bullion dressing, anode casting, and cathode melting and the electrolytic tanks are all under one roof (the same once used for thermal refining). In adjacent rooms the conversion cabin and the sections for electrolyte preparation, recovery and washing of anode slimes are located, while the metallurgical treatment of this slime is done in another section.

#### The electrolyte

39. For more than four years the electrolyte maintained the characteristics perfected in the pilot plants and that it: Pb = 80-85 gr/lt. ; free  $\text{H}_2\text{SO}_3$  = 45-50 gr/lt. ; total  $\text{H}_2\text{SO}_3$  = 130-140 gr/lt. ; tannic acid = 1-2 gr/lt. In this period no sensible changes from the pilot plant were noted. The electrolyte did not change because of the accumulation of impurities and, without being heated or cooled, maintained a temperature varying from 30 to 35 degrees C. according to the season. However, it was noted that with a current density above 90-95 A/sq.m. a continuous, even if modest, decomposition of lead

sulphate with the formation of amorphous sulphate and consequent precipitation of lead sulphate took place. This loss, better individualized, is added to the mechanical loss through the anode slime and the inevitable losses and spillage.

40. The tendency of the lead ion concentration to increase, owing to the higher anode efficiency over the cathode efficiency was found not only balanced by the mechanical loss but inverted because of sulphate decomposition.

41. All test set reproductions in a running and continuous sulphuric acid and litharge electrolysis for the preparation of fresh, re-integrating electrolyte. The total losses were: 4 kg. of sulphuric acid and 2.5 kg. of litharge per ton of refined lead. The sulphuric acid and lead losses by decomposition of the sulphate increased rapidly if the current density went above 100 A./sq. d. At this current density, the average voltage per cell was 0.75 V. The DC energy consumption was 210 kWh per ton of cathode lead.

42. The cathode deposit was thick, compact, and regular and allowed the cathode to be immersed for a period of seven days. The anode remained immersed for fourteen days and the slime blanket remaining after lead extraction covered well to the non-corroded area. The purity of the refined metal was excellent.

43. On the whole, electrolytic refining with sulphuric acid was simplified as secure and efficient even on an industrial scale even though it is undoubtedly inferior to the fluoboric electrolyte as far as concerns conductivity and the possibility of using a higher current density.

44. The comparison between sulphuric and fluoboric electrolyte was attentively and exhaustively studied during the research phase and the pilot activity, but even though the superiority of the fluoboric electrolyte appeared evident, its adoption was impossible, given the impossibility of obtaining an economic and sufficient supply of hydrofluoric or hydrofluoboric acid in quantity.

#### Conversion to hydrofluoboric electrolyte

45. At the end of 1960, a large quantity supply of hydrofluoboric acid was made available near San Davino, obtained as a by-product in a phosphate fertilizer factory and the conversion from sulphuric to fluoboric electrolyte was taken into consideration.

46. At the end of a brief test cycle, the gradual conversion from one electrolyte to the other was definitely proved possible. That was accomplished by completely suspending every new addition of sulphuric acid and by starting to add

hydrofluosilicic acid in the plate, having previously neutralized the free sulphuric acid with lithium. The electrolyte from 100% sulphuric electrolyte containing 10 g/lit. of free  $\text{SO}_2$  and 1.0 g/lit. of total  $\text{SO}_2$  to 100% fluorosilicic electrolyte containing 10 g/lit. of  $\text{F}_2$ , 10 g/lit. of free  $\text{SiO}_2$  and 1.0 g/lit. of total  $\text{SiO}_2$ , have shown over a period of 10 months during which time there was a steady electrolyte made up of a substantial amount of lead sulphate, an increasing amount of lead fluorosilicate and free fluorosilicic acid. The progressive disappearance of the sulphuric acid clearly took place by decomposition of the sulphate and was analytically controlled by finding free  $\text{SO}_2$  in solution and  $\text{F}_2$  also collected in the bottom of the tanks. There were no accumulations of any kind during the entire transition period. In addition, agents, namely acid, used for sulphuric electrolyte, was replaced by glass and gelatin. From this substitution caused no trouble in the electrolyte as evidenced in the characteristics of the cathode deposit. But it was clearly evident that while glass plus gelatin or glass plus hydrofluoric acid and fragile cathode deposits with sulphuric electrolyte, they caused a thick, plastic and soft deposit that caused an deformation of the cathode with fluorosilicic electrolyte. The cathodes could thus remain used and for one day more at the same current density or the same number of days with a higher current density. The conductivity of the electrolyte showed a continuous increase, parallel to the increasing concentration of  $\text{SiO}_2$ . Keeping the current density, the concentration, the temperature, and the lead concentration of the electrolyte constant, the average mileage per cell dropped from 0.7 V at 100% sulphuric to 0.5 V at 100% fluorosilicic, touching all the intermediate values in the scale in the 10 months.

17. The characteristics and differences between the two electrolytes can be summed up as follows:

18. 1) The selective process of the separation of lead is substantially the same. It is also a very high level of purification.

19. 2) The conductivity of the fluorosilicic acid is much higher and the average mileage applied to the cells, all other things being equal, is less than half.

20. 3) Lead fluorosilicate is even more stable than the sulphate. The latter begins decomposing if a current density of about 10-15 A. eq. is used, while that does not happen to the fluorosilicic electrolyte even at a current density of 200 A/eq.

31. d) The fluxolite electrolyte permits operation at a current density of between 150 A/sq. ft. and 250 A/sq. ft. at the same time, according to the composition of the anodes to be refined. The highest current density possible for sulphate, in the most favorable conditions, is 250 A/sq. ft.

32. 3) The fluxolite electrolyte, being more stable, does not require lead acid consumption and the acid consumption is less than with the sulphate electrolyte.

33. 6) Fluxolite acid, usually obtained as a by-product of phosphate fertilizer production, costs much less than sulphuric acid. This saved sulphuric acid clearly is found in the fluxolite electrolyte, these advantages are:

- a) lower power consumption per ton of refined lead - a lower reagent cost (oxide and coils of lead) with features of lower consumption and reduced of lower unit price.
- b) lower plant cost, given that the same number of coils can produce twice as much.
- c) lower labor cost because of the greater weight of the cathodes.

#### General Features

34. The two service plants are furnished at a current density of 150 A/sq. ft. permitted by the maximum intensity of 2500 A furnished by the rectifier. Under such conditions, the daily production with 120 coils is 100 tons per day. The case refinery building is divided into three sections, each 14 meters wide and 30 meters long. Each section has a six-ton crane whose characteristics are: bridge travelling speed = 30 meters per minute; load raising speed = 15 meters per minute.

35. The tanks are arranged on a platform 2.5 meters above the ground. The floor under the tanks is concrete protected by asphalt. The working floor at the height of the coils is to steel mesh with a heavy substance. The space reserved for waste sorting and cathode cutting is surfaced with steel tiles.

36. The coils are arranged in equal numbers in the three sections, each of which contains a group of 12 coils in line with their longest sides parallel and 4 of these groups are in their turn at 1 and 2; thus there are four banks of coils per section and the single separator by corridors, with a total of 144 coils per section, of which 2 are for slime removal and reserved waste cutting. There is a total of 432 producing coils.

37. The standard coil is 270 cm. long, 95 cm. wide, and 100 cm. deep and is



cells with concrete 7 cm. thick lined with 2 cm. of P.V.C. In the bottom there is a drain with an anti-siphon 60 cm. long. In the longer edges of the cells there are embedded strips laminated with rubber supporting the bars and spacing insulators for supporting and spacing the anodes and cathodes. The bars have a section of 1 1/2 cm. by 1 1/2 cm. The cells are electrically in series. The electrolyte (anodes and cathodes) is parallel.

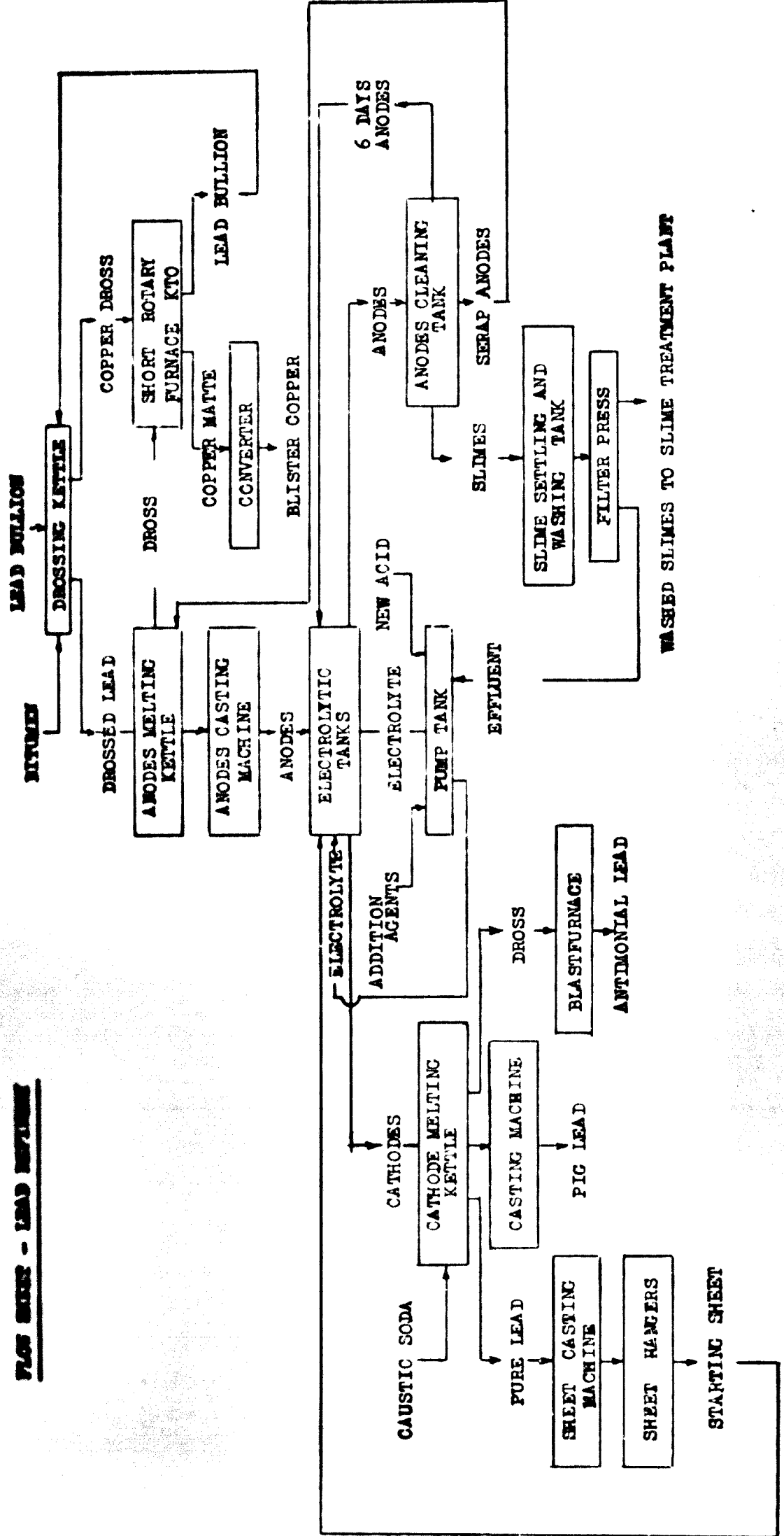
The tank with electrolyte is kept in constant circulation through the cells to keep the concentration of Pb and  $\text{SO}_4\text{Pb}$  constant in all parts of the cell.

The lead concentration tends to increase at the bottom of the cell while the free acid concentration tends to increase at the surface. In each row, there are in practice ten rows of 12 cells and ten double rows of 12 cells in each section; the cells in the single rows have independent circulation; in the double rows there are connections of ten cells with the factor at the head of the first and the discharge at the end of the second. The electrolyte reaches the cells with a flow of 12-14 liters per minute by means of P.V.C. pipes that run along the ten rows; from these pipes the feeding pipes, corresponding in number to each cell or group of ten cells, which discharge at the surface of the liquid, lead out.

The electrolyte comes out of the opposite ends of the cells by means of siphons and discharges into open canals, they run running along the cells, which carry a storage tank from which a pump sends it back to the cells. The storage tank has a useful capacity of 30 cubic meters. The pump, has a capacity of 4000 liters per minute, the motor and shaft is brass and the housing is stainless steel. The electrolyte temperature varies from 15 to 25 degrees C. without cooling heating or mixing. The composition of the electrolyte, which is kept under the following: Pb = 70-75 g/lit., free  $\text{SO}_4\text{Pb}$  = 70-80 g/lit.; total  $\text{SO}_4\text{Pb}$  = 135-140 g/lit.; is controlled by adding, during circulation, electrolyte addition agents or acid. Silver and gold (a light colored sulphate) are prepared as mentioned in item 2.3.2. Lead tanks and are added by gravity to the pump tank. Additions of new acid are also made by the pump tank.

2.3. During operation, the percentage of Pb in the electrolyte tends to increase as slowly, since the anode efficiency is slightly greater than the cathode efficiency. In practice, the true economical losses and the inevitable slight losses of fluorinated as residues in the anode since they the lead content of the electrolyte constant.

**PLANT SKETCH - LEAD REFINING**



Bullion dressing and anode Casting

59. Bullion from the blast furnace having the average analysis of 1,7% Cu - 1,2% Sb - 0,2% As - 0,07% Ag - and 0,07% Bi is gathered in a three-ton ladle and transferred to a 120-ton kettle where it is dressed for copper by cooling in two stages. In the first stage the temperature is lowered to 400 degrees C. From 10 to 15 kilos of bitumen are added to the kettle with mechanical stirring that lasts about 30 minutes, until the dross becomes completely powdery, allowing removal. Then the temperature is lowered again as close as possible to the melting point. Then 8 or 10 more kilos of bitumen are added, the bath is stirred for another 20 - 30 minutes, and the dross formed in this second stage is removed. The dross is easily handled with a compressed air bucket. The dross has the following average composition: Pb = 60% ; Cu = 23% ; As = 5% ; Bi = 0,04% ; S = 5% ; . In the dressed lead, copper goes down to 0,03%.

60. The dross is treated by soda process in a short rotary furnace 4 x 3,5 meters to recover copper as a matte-speiss mixture having about 60% copper and 15% lead.

61. The anode casting plant (fig.2) is made up schematically of two kettles (A - A) with a capacity of 90 tons of molten lead, each of which, by means of a screw tap at the bottom, can feed a small 3 ton kettle (B). On the bottom of the small kettle there is a conical drain, where a pipe reaching above the casting wheel (C) is attached. On the casting wheel there are 18 anode molds arranged in a circle. The conical drain is usually closed by a vertical shaft that can be raised or lowered by means of an electromagnet thus opening and closing the flow of lead which, guided by the pipe and a short horizontal canal, reaches the molds.

62. With the wheel stopped, one mold is found under the end of the casting canal of the kettle. The lead flows from this to the mold, filling it to the desired anode size. At this point the flow is arrested automatically and the wheel, after several second' hesitation, revolves and stops automatically when the next empty mold is under the end of the canal, provoking another flow of lead. After successive movements the anodes, cooled by jets of nebulized water, are pushed out of the molds in such a way that as the rotation proceeds in correspondence with a special conveyor (D) they can be taken one at a time, raised, and put onto a collecting conveyor (E) on which they are spaced at a distance of 10 cm. from each other. The conveying and ordering of the

anodes is done automatically. From the collecting conveyor the anodes are taken by crane in groups of 25 to be put on a last, large conveyor whose job is to distribute the anode packages to the electrolytic cell section.

63. At San Gavino, for a daily production of 105 tons of marketable lead, 700 lead anodes of 200 kilos each are put into the cells. In every day 140 tons of anodes are cast of which about 40 tons equal to 30% return to the kettle after a twelve-day corrosion cycle, while the rest is subdivided between market production (70%), anode slime (1%), and cathode re-casting oxides (1%).

The anodes are 620 x 740 mm. under the lugs and are 15 mm. thick.

64. The small 3 tons kettle, with a truncated cone section and resting in an oil-fired furnace, has the function of regulating and being the lead that continually comes out from one of the 30 tons kettles, while the flow from the small kettle is intermittent. In on the inside the level of the metal changes continually and predictably. The central drain (a) is closed by the plug (b) attached to the shaft (c) controlled by two rollers and weighted by the block of iron (d). The shaft is attached to the lever (e), having fulcrum (f), which can be moved back and forth by means of the wheel (g). The electromagnet (h) is attached to the other end of the lever. The pull of the electromagnet causes the raising of the shaft which, being able to move the fulcrum of the lever in two directions, can have its course changed, obtaining the flow as well as the exact regulation of the lead flow. The closing and opening of the electric circuit of the electromagnet takes place automatically. The mold adopted is shown in fig. 3. The edge of the mold is broken in a  $\frac{1}{2}$ " for a distance of 150 mm. and then closed by a tooth (b) of the same length bladed at the edge. The tooth, whose profile is shown clearly in the figure, is along the bottom of the mold. This projecting part is covered by the metal and, once the anode solidifies, by rotating the tooth 90 degrees around the hinge acting on the axis (c) connected to the tooth, undercut and partial raising are obtained. This mold has been designed especially to make out the anode without deforming it.

65. The casting wheel is a circular platform with a diameter of six meters sustained by 16 rollers. Around the wheel there are 18 blades each of which occupies an arc of 20 degrees. The casting time for the anode is twelve seconds. The productive capacity is two anodes every 2" seconds. The hourly production is 144 anodes or 28 tons per hour. The best casting temperature is about 350 degrees C.

64. Referring to fig. 2, the mold filling takes place in position I.

The tooth of the mold is levered and its maneuvering axis is blocked by the spring on the platform. Two copper electrodes attached to a rocking device (P) are suspended on the mold. In the casting phase, while the kettle's electromagnet causes the raising of the closing shaft, a small electromagnet (I) attracts one end (a) of the device in such a way that the point of the electrode is at the same level as the anode thickness desired.

Once the lead in the mold reaches the fixed level, it closes a circuit between the two points of the electrodes, causing the opening of the circuit of the electromagnets and the closing of the circuit of the wheel's motor. Thus the shaft is lowered, arresting the lead flow and the electrodes rise from the mold to permit its passage. After three movements in 75 seconds, the anode, still partially partly, reaches position II where it is lightly and uniformly sprayed with pulverized water from three pulverizing nozzles. A gradual spraying of water allows uniform cooling of the entire anode, avoiding break internal tension which would immediately deform it. The anode reaches position VII at a temperature slightly higher than 100 degrees C. at that stage cut can begin.

Until now, the teeth of the mold have been closed and the case have been vertical as in fig. 3. On a special cam track under the wheel begins revolving in a vertical and radial direction.

This cam track is located in an arc of 100 degrees and engages the case, causing the continuous and gradual rotation of the teeth until they have rotated 20 degrees when the mold is in position VIII and the anode is raised as shown in fig. 4. Then the lifting conveyor, which lifts the anodes by the lugs and takes them away, comes into action. Once the weight of the anode is removed, the tooth goes down again, aided by the weight of the case and the counter-weight applied to it. The case is blocked by the spring X and the tooth is once again closed. As already indicated, the anode reaches position VIII when the anode is already loaded into its lugs raised and the wheel stopped, while the small bottle is in the casting phase. Then the lifting conveyor comes into action. This conveyor is made up of two sides having a profile as shown in fig. 5, each made up of ten frames in which a space or case. Each side, 7 meters long, holds up the ends of ten transversal, equidistant rods, to each one of which ten anodes of a thickness slightly superior to the width of the anode under the lugs is placed. In the stopped position, the ends of a pair of anodes are about 2" in case the raised anode lugs. When the wheel has traveled of 75 degrees of the 20 degrees of every regular and recurrent shift, the

conveyor moves and a pair of hooks come down on an anode to be lifted, lifts it, and puts it on the collecting conveyor.

67. The collecting conveyor is made up of two chains having links adapted for receiving the anode lugs brought by the lifting conveyor. The chains have a gauge of 10 cm. equal to the distance between the center lines of two anodes spaced for entering the cells. The collecting conveyor is usually not in motion. As soon as an anode rests its lugs on the corresponding links of the chain, the chains advance one step, advancing the anode 10 cm., leaving room for the next anode corresponding to the point where the hooks of the lifting conveyor come down. There is room for 30 anodes on this conveyor

At intervals of 625 seconds, 25 anodes at a time are picked up without interrupting the casting cycle by a rack attached to a 5 ton crane and are put onto a special conveyor for distribution to the electrolysis cells. This is the only time that the direct intervention of the only worker in the section is required. From what has been described, it is evident that the perfect synchronization of all movements allows the automatic production of any number of anodes without personnel increases. Besides this advantage of requiring little manpower, there is also the great advantage, which is derived from all automatic plants, of repeating each casting cycle under identical conditions for which, since subjective judgments as to the filling of the molds, and the sprinkling of water are eliminated, all the anodes are of the same weight and are perfectly vertical.

68. Each anode is supported in the cell by its lugs, one of which rests on the bus-bar while the other is insulated from the bus-bar on the opposite side by hardwood insulators. The immersed area of each anode face is  $62 \pm 70$  cm. The cell load of 25 anodes weighs about 3 metric tons. Following electrolysis, the anode weight is about  $\frac{1}{2}$  of the original. This anode is washed free of slime and melted in one of the ten 30 ton kettles and previously in the same kettle into which the treated solution is pumped and from which the anodes are cast. The anodes have the following average composition: 1,  $\frac{1}{2}$  Sn - 0,  $\frac{1}{2}$  As - 0,0  $\frac{1}{2}$  Cu - 2,  $\frac{1}{2}$  Ag - 1,0  $\frac{1}{2}$  Bi

#### LABORATORY

69. The immersed area of each cathode face is  $65 \pm 75$  cm. At first, the system of preparing the cathode starting sheets by electrolytic depositing on stainless steel sheets from which the lead sheets were stripped over 48 hours

at a thickness of about 2 mm. was used. For that purpose 50 of the 336 cells were equipped with stainless steel cathodes and 600 cathodes per day were extracted in rotation which gave the 1200 cathode starting sheets necessary. The stripping was very laborious and required much man-power.

70. This system was changed to that of the preparation of the cathode starting sheets by continuous casting of a thin strip of lead 0,8 - 1,0 mm. thick by means of a water-cooled drum revolving in a bath of molten lead.

71. This system, used for the first time at Trail by the Cominco, has been perfected and greatly simplified at San Gavino. The drum has a length of 65 cm. and revolves around a horizontal axis at r.p.m. 10. On the drum liner, half-way down the length, there are two notches with the dimensions of 250 x 300 x 20 mm. deep. The drum, cooled by internal water circulation, revolves above a basin in which a constant level of molten lead is maintained with the drum face immersed to a shallow depth. A thin layer of metal adheres to the cold liner and on being pulled, becomes a continuous sheet whose width is determined by the length of the drum and whose thickness is controlled by regulating the depth of immersion and the temperature of the bath. Given the presence of the notches on the drum, the lead sheet comes out as a sheet with openings of 250 x 300 mm. that repeat every 110 cm. in the center. On the ideal prolongation of only one side of each notch, along the generatrix of the drum to one side and the other of the notch itself, there is a small light incision that determines a very slight gap in the forming sheet because of which, instead of a truly continuous sheet, individual sheets of lead cut to the desired size and having a rectangular form with two prolongations for hanging on a copper bar are directly obtained from the drum. The cathode starting sheet machine is operated by two men and produces 20 individual sheets per minute i.e., 1200 sheets per hour. In practice at San Gavino, this machine works an eight-hour shift every 6 days.

72. Before going into the cells, the cathode starting sheets must be hung firmly on the copper bars and must be as flat and as vertical as possible to avoid short circuits. Both goals are reached by using a machine composed of two strong, vertical iron plates hinged at the bottom. One of them is fixed in position and one is movable. The lead sheet is hung on its copper bar with its lugs wrapped around it and inserted between the iron plates, one of which, propelled by a compressed air piston, slides and perfectly straightens the lead sheet. At the same time the lead sheet is stapled to the copper bar.

Two men are sufficient for readying all the cathodes needed for one day in 8 hours.

73. As the cathode starting sheets are prepared, they are arranged, spaced at 10 cm. and readied for the cells on chain conveyors installed under the working floor in the corridor between two rows of cells.

In each of the three sections there is a sheet straightening machine and a 40 meter conveyor capable of receiving 400 cathodes. The cathodes are taken from the chain conveyors in packages of 24, the number used in each cell, by a crane through a hole in the working floor.

#### Cell Operation

74. Every cell contains 24 cathodes and 25 anodes. The cathodes have a life cycle of 6 days and the anodes of twelve. Every day the cathodes are changed in 56 cells and the anodes in 28. Thus, the section has a daily need of 1340 cathodes and 700 anodes. To substitute them the cell is shunted so that all the cathodes and anodes can be changed at the same time. The individual cathodes have an initial weight of 6 kilos and an average weight of 80 kilos after a six-day immersion. The cathodes coming from the cells are put, with their copper bars attached, on a special chain conveyor that runs at the head of the row of cells crossing and connecting the three sections of the building.

This conveyor, on which the cathodes are washed with jets of water, takes them to a fixed point where a band-saw cuts them away from the copper bars. The cathodes then fall onto a steel plate conveyor that takes them to one of two 120 ton kettles, where they are melted. The copper bars are collected in a different place, pickled in a diluted nitric acid solution and then rinsed with water and machine oil before being used again.

75. The anodes are arranged, in packages of 25, just as they come from the casting plant, on another special conveyor located at the head of the row of cells and linking the three sections of the building. This conveyor is fed, at the head situated in the section where the cast anodes are found, with packages of 25 anodes. As they are produced, the conveyor moves ahead until there are 28 packages of anodes distributed at the head of the three sections within reach of each section's crane. The packages of new anodes go to the cells while the corroded anodes return to the conveyor to be taken back to the re-melting kettle.

#### Slime Handling

76. Before the corroded anodes go to the re-casting, the slime and the



electrolyte it soaks up must be recovered. To limit fluosilicic acid consumption, all the causes of systematic loss must be avoided and the anode slime must be carefully washed. In lead to be refined there is such a percentage of impurities that as the anode dissolves they form a spongy, compact layer weighing  $2.5 + \frac{3}{4}$ % of the metal it was originally incorporated in, having however, the same volume. If the sum total of impurities is inferior to 1%, the anode slime is incoherent and easily detaches itself from the metal support, causing electrolyte contamination and cathode deposit contamination. If the sum total of the impurities is about 2%, the layer of slime preserves the same shape as the new anode. It is a true metallic sponge through the pores of which the lead ions must pass in their migration from anode to electrolyte to cathode. The solution held by the slime has much lower percentage of free acid than the circulating electrolyte and a much higher percentage of lead fluosilicate. There are two clear reasons why the voltage rises in the cells as the anodes corrode: the gradual rise in the ohmic resistance of the growing slime layer and the counter-electromotive force caused by different concentration of the circulating electrolyte and the electrolyte in the slime. Thus there is a gradual rise in the cell voltage from 0,3 initial volts with a new anode to 0,45 + 0,50 final volts when the slime layer has reached a certain thickness.

77. To avoid an excessive increase in the slime layer thickness and the consequent increase of voltage in the cells and an abnormal enrichment of  $PbSF_6$  in the captive electrolyte, the slime is removed after a 6-day corrosion period. This is done using three slime removal cells which allow the removal and recovery of the slime of a complete package of corroded anodes in a very short time. It is a type of cell on which there are, horizontally arranged, in the same position and at the same distance, as many rubber tubes as there are cathodes in the common cells. The tubes have a flattened cross-section, are activated by small, flat iron bars, and are attached to fixed anchors on the two long sides of the cell. Each tube is closed at one end and has the other end connected to an air compressor. The corroded anode packages are lowered by crane into these cells so that each anode falls between two tubes. When the anode package is lowered and its lugs are resting on the edges of the cells, compressed air is sent into the tubes which swell until each anode is tightly imprisoned between two tubes. Raising the package with tubes swollen, the slime layer is scraped off the anodes and stays in the cells.

78. The anodes are acceptably "clean" after this scraping, which recovers a good 97-98% of the slime layer. The recovery of the remaining 2% and complete cleaning are accomplished by immersing the anode package in a cell full of water, acid because of the presence of fluosilicic acid, kept bubbling by a compressed air jet. A certain amount of slime accumulates on the bottom of this cell in time while the water is progressively enriched with acid and lead until it reaches a content very similar to that of the circulating electrolyte to which it is periodically added. After slime removal, the 6-day anodes are returned to the cells and the 12-day anodes are returned to be re-melted.

79. The slime removal and washing cells have a drain in the bottom, closed by an anti-acid valve, and are attached to pumps and to a tube by means of which the slime water (containing about 15% solids) is pumped to a set of 15 cubic meter tanks in which decanting and washing takes place before passing on to a string discharge rotary filter, the filter active surface of which is 10 m<sup>2</sup>. From the filter, a slowly diminishing liquid concentration of fluosilicic acid and lead fluosilicate which returns to the depositing basins to join the circulating electrolyte and a solid cake of slime with 35-40% moisture are obtained.

80. For the first collection, decanting, washing and filtering of the slime, there are six 15 cubic meter tanks of which one in turn is designated to receive one day's production of slime. The other 5 alternate every day in one phase of a 6-day washing cycle, the same as the cathode substitution cycle.

For pumping the slime water and electrolyte counter-current from the removal and washing cells to the decanting and washing tanks and from these to the filter, ebomite pumps are used. The slime that accumulates at the bottom of the cells is also pumped to the decanting tanks. This is done by connecting the discharge valves at the bottoms of the cells to the slime pump. In this way the slime is removed every three months at the rate of three <sup>cells</sup> a day.

81. The filtered slime is accumulated under the stull of the tanks and filter for the successive metallurgical treatment. Besides the 6 slime washing tanks, there are three other tanks in the same sector for the initial electrolyte preparation, for containing the fluosilicic acid to be added periodically to the cycle, and for dissolving the addition agents (glue and goulac) to be added daily to the electrolyte at 40 kg. per day each.

82. For all the activities of the cell sector, 6 men are needed: 4 for changing the anodes and cathodes, 1 for filtering the slime and 1 for general services such as cleaning copper bars, preparing "addition agents", etc.

### General Rolling and Ingot System

83. There are ten 120 ton orange pool kettle with oil-fired furnaces for anode melting. From the casting conveyor the heavy cathodes, after recovery of the copper bars, fall onto a steel plate conveyor that gives them to one of the ten melting kettles. When a kettle is full, several sizes of anode rods are added in a ratio of 0.7 to 0.9 kg/ton of metal and, at a temperature of about 450 degrees C., a mechanical stirrer agitates the bath for about 30 minutes, until a light layer of completely dry and loose oxide is formed on the surface. Lead casting from the kettle is done by means of a pipe with a tap or a small centrifugal pump.

84. An automatic casting machine designed and built at the Service is used for making the ingots. The casting machine is made up of a strong section iron frame that holds guides on which special chains carrying cast iron molds for forming ingots of caustic shape weighing 50 kilos run. The chains and molds (74 of them) form a continuous conveyor moved by a pair of gears connected by a 3 HP motor. The length of the machine is 7 meters. At the head of the machine, immediately above the molds, there is an iron basin in the bottom of which there is a 20 mm. drain. This drain is closed by an iron shaft connected by a system of levers to a pneumatic cylinder whose piston, rising and falling, causes the raising and lowering of the shaft, thus opening and closing the drain from which the metal flows into the molds. The air for the pneumatic cylinder is intercepted by an electric valve. The filling of the molds takes place with the machine stopped, when the center of the mold is directly below the basin casting drain. There is a pair of levered copper electrodes to limit the level of filling exactly. When the molten metal reaches the level of the electrodes it closes the circuit. Then the electric valve comes into action, acting on its pneumatic cylinder causing the lowering of the shaft, interrupting the flow of metal. At the same time, current reaches the motor, putting the conveyor in motion until the next mold reaches the casting drain at which point the motor stops and a new flow of molten metal begins automatically. The casting time for one ingot is 6 to 7 seconds. After fine forward movements of the conveyor the ingots, already solidified, are cooled by a jet of water before arriving under a mobile hammer which automatically prints all the needed particulars of the lead shipment on the ingot. At the end of the conveyor's run, the molds, following the chain, are turned upside-down, causing the ingots to fall out onto a specially shaped slide which overturns them and puts them in the right



**Slime Treatment**

**Slime Solids**

28. Slime solids treatment takes place in a dedicated building 28 : 60 meters in length there are ten large 2700 short rotary furnaces 1, 20 x 4 meters, three 12 ton converters, ten reverberating furnaces, and two large furnaces. The two short furnaces are followed by ten independent bag houses. The other furnaces and the converters are attached to a furnace. In the building, besides slime solids treatment, copper brass rolling and copper brass connecting are carried out as well.

29. The slime from the filter has a moisture content of 75% of 6. It is concentrated under a shed where it loses a large part of its moisture, both by natural loss through evaporation and because of the development of heat due to the spontaneous partial oxidation of the slime mass. The main goal of slime solids treatment is the most integral recovery possible of slime and bricks as well as the very small fraction of gold contained. Recovery is measured approximately as percentage yield with a very variable content of 5%. The average composition of the slime solids is as follows: 28 = 25% of 6 ; 29 = 40% of 6 ; 30 = 10% of 6 ; 31 = 12% of 6 ; 32 = 0,10% of 6 ; 33 = 10% of 6 as a 0,001% of 6 ; The attached diagram shows the slime cycle.

30. 1) The first phase is a reducing melting at 950 - 1000 degrees F. with the addition of 2% of coal from which is obtained: a) a brass composed of 28 and 30 oxides. b) a scum in which all the Cu, 28, 33 and 34 present in the slime are collected together with a part of the 28.

The melting of the slime can be done in various types of furnaces. Among these types one the most suited is the short rotary furnace, used at the factory.

31. Typical characteristics of slime solids even if dry, <sup>Y</sup> its state of extreme oxidation, low melting point and consequent low specific heat, for which a relatively small quantity in weight is a sufficient mass heat blocks up the furnace into which it is put and that begins to melt rapidly at the surface, forming a crust that heat can pass very very slowly towards the interior of the mass. Only by stirring and mixing the mass can <sup>Y</sup> a first liquid mass and progressive melting be generated. After melting has commenced, there are ten well-differentiated layers of oxidation: a surface oxidized slime and a lead containing slag whose residual percentage of precious metals, 33 and 34, is a function of the reduction grade of the charge and of the possibility of capturing

ing and maintaining completely separate the two layers.

92. The rotating KTO furnace has all the prerequisites for the most efficient, rational, and economical melting of anode slime. The continuous rotation of the furnace provides for, from the first loading, the continuous re-mixing of the mass, impeding formation of crust and isolating accretions. KTO's possibility of tapping the molten charge at various levels allows the accurate removal of the single molten products, accomplishing complete separation and avoiding one part's holding onto a fraction of the others. The short rotary furnace is oil-fired and has a lining of 12 inch magnesite bricks. It has a melting capacity of 15-20 tons of slime in 24 hours.

93. Typical slag and metal assays are shown in table II below:

TABLE II

Assays of Short Rotary Furnace Products

	Pb%	Sn%	As%	Cu%	Bi%	Ag%	Au%
Sb - Pb slag	20-25	45-50	2-3	0,1	0,030-0,004	0,01	-
Baghouse dust	3-4	70-75	18-20	-	0,08-0,1	0,05-0,06	-
Metal	30-40	15-20	2-3	2-3	10-15	12-16	0,004-0,03

94. 2) The second phase of the slime cycle is the oxidation of all the antimony and arsenic still together with the noble metals in the silver alloy. This oxidation takes place at the expense of a good part of the lead and a percentage of the bismuth and copper contained. The operation can be accomplished in the same KTO used for slime melting by introducing a series of pipes attached to a network of compressed air. But usually one of the 3 copper converters is used. The Pierce-Smith type of converter has 10 tuyeres and a lining of magnesite brick. It is initially charged with 10-12 tons of metal at 800-900 degree C. and immediately given air. The oxidation is accomplished in 3-5 stages followed by slag tapping and the adding of new, solid metal.

95. In the first stages, carried out at a temperature of 900-1000 degree C., all the arsenic and about one-half of the antimony are volatilized. The dust collected in this phase together with that of slime melting are to be treated for the recovery of the antimony. Air blowing, slag tapping, and addition of fresh metal follow each other (stages 3,4,5) until the converter is full of metal from which all the antimony has been removed. At this point, the following composition can be confidently assigned to the metal still in the converter:



20-25 Ag ; 0,5-0,8 Sn ; 20-25 Bi ; 20-25 Pb ; 0-10 Cu.

The slag is usually composed of Pb and Sn oxides.

96. The final stage consists of another air blowing at a temperature of 1000-1100 degrees C that is continued, at the expense of oxidizing a great part of the lead and bismuth, until the percentage of Ag reaches 20-25. The slag formed in this last stage contains from 20 to 25% of the oxides remaining present in the slime.

97. Typical slag and metal assays are shown in Table III:

TABLE III

Assays of Converter Metals and Slags

	Pb	Bi	Sn	Ag	Cu	Fe	Mn
20-25 Ag	20-25	20-25	0,5-1	0,1-0,2	0,2-0,4	0,05-0,1	-
Bi slag	25-30	1-2	-	1,2	20-25	0,1-0,2	-
Total	20-25	-	-	0-2	25-30	20-25	0,05-0,15
Slag	5-10	0,5-10	5-6	-	0,5	0,1	-

98. In the third stage of the slime cycle there is the final concentration of silver and gold in anodes of 99-99,5% Ag plus Au. For that reason the silver metal of the converter, concentrated at 20-25% Ag, passes into a cupel furnace in which, with the progressive addition of lead, all the bismuth and copper still present are oxidized and removed. The lead added to the cupel furnace is about 20% of the metal treated.

The operating technique of the cupel furnace is well known. The cupel furnace used is heated by ether circulation. Its capacity is ten tons of dried. Bismuthiferous litharges and lead of 99,5% Ag plus Au are obtained from the cupel furnace. The lead is used with 5 kg. anodes for further electrolytic refining.

TABLE IV

Typical Assay of Cupel Products

	Pb	Bi	Sn	Ag	Cu
Pb - Bi slag	20-30	0-2	20-25	1-1,2	-
Lead anodes	0,15-0,2	0,1-0,15	0,1-0,15	99,5	0,1

99. Of the silver and gold that enter the electrolytic refining cycle with the anodes, 0,1% goes to the lead cathodes, which have a silver percentage of about 0,0002%, and 99,9% is found in the anode slime from which 20-25% is directly recovered.



1 -  $\text{Ag}$  and  $\text{Au}$  are lost out of the melting cycle temporarily and distributed as follows:

	$\text{Ag}$	$\text{Au}$
1) In the Pb-Sn alloy melting slag	0.12	0.12
2) In the antimonial alloy melting slag	0.05	0.05
3) In the converter Pb-Sn slag	0.1	0.1
4) In the converter transformer slag	0.05	0.05
5) In the converter antimonial slag	0.1	0.1
6) In the Super Furnace litharge	1.00	1.00
7) In the Super Furnace slag	0.05	0.10

100. The Pb alloy melting slag and the antimonial alloy melting slag and the converter slag constitute the starting products for extracting antimonial lead. In every case, the silver and gold in them are to be recovered.

101. The silver and gold contained in the converter slag, in the litharge and in the Super Furnace slag are recovered by means of partially reducing molasses that concentrate the two metals into a Pb-Sn alloy from which

the standard treatment and extraction cycle begins. From this alloy at least 75% of the  $\text{Ag}$  and  $\text{Au}$  are separated and recovered. The total loss of  $\text{Ag}$  and  $\text{Au}$  is:

	$\text{Ag}$	$\text{Au}$
Loss into antimonial	0.12	0.12
Loss into Pb-Sn slag	0.05	0.05
Loss into transformer slag	0.05	0.05
<b>TOTAL</b>	<b>0.22</b>	<b>0.22</b>

102. In these severely indistinguishable and uncontrollable losses due to either the failure caused by essential deficiencies of the ingresses or control filters on the furnace, the converter, and the Super Furnace, and those owing to loss of insufficient recovery of the waste slimes. These losses are estimated at 0.10 to 0.15 of the initial silver. If the better  $\text{Ag}$  and  $\text{Au}$  recovery efficiency is given 75%

**RECOVERED SILVER**

103. The recovery contained in the waste slimes is distributed among the by-products of slime treatment as follows:

	<u>Antimony %</u>	<u>Percentage of total lead %</u>
Slime settling antimony slag	67-70	60
Slime settling antimony dust	70-75 )	23
Converter settling antimony dust	67-70 )	
Converter settling antimony slag	32-35	7

104. More than 90% of the antimony is collected by-products with high Sb concentration. To recover it, a total reduction of the sludge and dust sized together with the residue obtained from anode melting is used. An antimonial lead containing 15-20% antimony and 1-2% arsenic, with copper, bismuth, and silver impurities is obtained. By the successive dilution with refined lead, antimonial lead having: 3-15% Sb ; 0,005% Cu ; 0,02% As ; 0,005% Bi ; 0,005-0,01% Ag is obtained. This lead is used in the melting of more than 7000 tons per year of cast. The operation is done in a blast furnace during specially scheduled programs.

Bismuth Concentration

105. 95-98% of the bismuth initially present in the anode sludge is found in the bismuthiferous converter slag and in the Capel furnace litharge.

By undergoing reducing melting, with an addition of 5% coal and 2-3% sulphur, three different products are obtained:

- a) A metallic Pb - Bi alloy in which all the bismuth, silver, and gold are collected.
- b) A matte that separates all the copper
- c) A Pb - Bi slag, practically sterile in Ag, to be re-used together with the antimony slag produced in other phases.

The alloy has the following average composition: 1-2% Ag ; 1-2% Sb ; traces of As ; 0,5-1% Cu ; 42-45% Bi ; 50% Pb. The series of operations that takes place from the Pb - Bi alloy to refined bismuth consists of substantially 5 phases: dressing, de-silvering, re-sintering, de-leading, and casting.

106. Dressing is carried out by cooling the molten alloy almost to the melting point and adding 0,1% sulphur and 1% coal dust under stirring. Thus sulphurization and liqueting of the copper contained is caused, which is removed with the dross that forms. The percentage of Cu is lowered to 0,01-0,0010%.

Then a mixture of cerate and sodium nitrate in equal parts is added to the bath whose temperature has been raised to 400 degrees C. This mixture is equal to 2% of the bath. The formation of dross is thus obtained, in which antimony collects as oxide. The antimony content of the dross reaches 15-20%,

while in the bismuthiferous alloy it goes down to 0,005 ± 0,01%. Dressing and antimony removal are accomplished in one 5-ton kettle.

107. For de-silvering, carried out by Parke's process, the bismuthiferous alloy is decanted into another 5-ton kettle of iron into which, at 500 degrees C., one addition of Bi - Zn - Pb alloy from previous operations and two additions of zinc are made, each one followed by cooling as nearly as possible to the melting point, and skimming. The silver content in the Pb - Bi alloy goes down to 0,0004 - 0,0006. The alloys skimmed after the first addition of zinc contain the major part of the silver and gold present in the Pb - Zn alloy. These Zn - Pb - Bi - Ag alloys with a high silver content return to the Cupel furnace and can be electrolytically treated for the direct separation of the noble metals. The zinc consumption is about 35 kilos per ton of treated bismuth. After de-silvering, a zinc percentage of about 3% is found in the Pb - Bi alloy.

108. Zinc and lead elimination is accomplished by letting chlorine gas into the de-silvered alloy, previously decanted into a 5-ton cast iron kettle and heated to 500 degrees C. The chlorine first combines with the zinc to form zinc chloride and only when all the zinc is eliminated does the formation of lead chloride begin. The chlorine, whose infusion lasts about 15 hours for three tons of metal, is consumed according to a rigid stoichiometric rapport with the zinc and lead, and allows the complete elimination of both.

109. After chloration, the molten metal is decanted into another cast iron, 5-ton kettle and air is blown into the bath to eliminate the chlorine and the last residue of lead and antimony. At this point the molten metal is decanted into another 5-ton kettle, covered with a layer of melted caustic soda, and cast in 10 kg. cakes.

110. The bismuth refined with the system described has the following composition: 0,0006 - 0,0012% Ag ; 0,0003 - 0,0010% Cu ; 0,0005 - 0,0010% Pb ; traces of Sb ; traces of As ; traces of Zn ; and 99,99% Bi.

The bismuth recovery efficiency is 9%.

111. There is a total of three men per shift in the slime plant. The same workers alternate in all the operations of the slime cycle, copper dross melting, and the copper blister production programs.

112. The productive capacity and the production of the San Gavino plant are as follows:

	Productive capacity	1968 Production
Lead Bullion	50,000 tons	25,000 tons
Electrolytic lead	38,000 "	27,000 "
Antimonial lead	10,000 "	2,000 "
Shot	10,000 "	7,300 "
Silver	50 "	22,000 kg.
Bismuth	100 "	9,000 "

### Electrolytic Lead Refining in Rumania

113. A plant for electrolytic lead refining, designed and built from Montepioni & Montevocchio on behalf of the Rumanian Government, went on stream in Copca Nica the first July 1968. That plant has an annual output of 40,000 tons of refined lead. The bullion, produced from the ISP plant running in the Usina Chimico Metalurgica of Copca Nica, has the average composition: Sb = 1,5% ; Bi = 0,2% ; Ag = 0,1% ; Au = 0,001% ; As = 0,2% ; Cu = 0,01%. The main product is electrolytic lead 99,997%Pb. Also the metals contained in bullion as impurities are totally recovered.

114. The average composition of electrolyte is Pb = 70 + 80 gr/lit. ; H<sub>2</sub>SO<sub>4</sub> total = 135 + 145 gr/lit. ; H<sub>2</sub>SO<sub>4</sub> free = 70 + 80 gr/lit. A standard cell with 30 anodes (230 kg. each) and 31 cathodes is used. The surface of the immersed part of the cathodes is 33 m<sup>2</sup>. With a current density of 160 A/sq.m. , current strength is 5,300 A. 208 electrolytic cells are installed. The production per day of a single cell is 170 kg. of refined lead. In a second time current density will be raised until 200 A/sq.m. The life of the anodes is 10 days and the life of the cathodes is 5 days. The package of 30 row anodes used for each cell has a weight of ca. 6,900 kg. 1,350 kg. of which (ca. 20%) are remelted.

115. Anode casting is effected in a separated section with two 100 tons kettles and with the same automatic casting machine used in Iasi Jovine. The section is operated by only one man. The time for casting each anode is 25 seconds and the production capacity of the plant is 144 anodes per hour, i.e. more than 15 tons per hour. From the collecting conveyor, the anodes are shifted by crane in stacks of 30 and placed on special tyre-trucks for transportation to the cells plant.

116. The 208 cells are distributed in two sections, in eight half-rows of 26 each whereby each section is served by a 10 tons crane.

The cells are built with reinforced concrete (8 cm. thick) and are clad with P.V.C. of 3 mm. in thickness. In each cell there is an independent circulation of electrolyte at a rate of 15-20 liters per minute. The temperature of the electrolyte is spontaneously maintained at 35° C. if the ambient temperature does not drop below 15° C. The cells are placed upon reinforced concrete supports 4 m. off the ground. Two Monel pumps of 5,000 lt/min. are provided for the electrolyte circulation, the electrolyte being pumped from two 20 m<sup>3</sup> holding tanks. The anodes arriving by truck from dressing and casting plant are stored on steel supports before joining the cells. Anode scrap returns to the melting kettles with the anode tyre-trucks.

117. Cathode starting sheets are made up from thin sheets of electrolytic lead (0,8-1 mm.). They are produced by means of the special device used in the Gervin and previously described.

118. Removal and recovery of the anodic sludge is also effected as in the Gervin, in two cells equipped with rubber pipes, followed from ten other cells filled with water acidified with fluoboric acid which is sprayed in a clean cycle against the immersed corroded anodes by means of a pump. The sludge is then pumped to an array of six vats of a volume of 15 m<sup>3</sup>. In which a cycle of decantations and washing operations is performed before it passes on to a 10 m<sup>3</sup> sludge discharge rotary filter.

119. For the melting of the cathodes, ten kettles holding 100 tons each are installed. From a collecting strand, the heavy cathodes fall on to a sheet plate conveyor conveying them to one or the other of the ten melting kettles, again recovering the current during their fall. The melting of the cathode rods is effected by the use of a casting machine similar to that constructed at the Gervin. The capacity of the machine is 15 tons/hour.

120. Slime treatment is carried out following the first sheet of the Gervin.

121. Consumption of reagents, power, fuel and complete reduced loss of cathode is that of the plant in the Gervin, and all the performances of the cathodes were rapidly recovered, so that heating and delivery of the plant were resumed just three weeks after the starting.

#### Electrolytic Lead

122. The planning of other electrolytic lead plants, with a capacity of 25,000 and 50,000 tons/year is on the way.

123. The standard cell has been increased at 34 anodes (230 kg. each) and 35 cathodes, for a minimum current density of 180 A/m<sup>2</sup>. A current strength of 7100 A will result and for a current availability factor of 96,5% the output of one cell per day totals 630 kg. of lead per day in cathodes. Assuming the number of working days per year to be 350 and the annual output to be 60,000 tons, only 280 electrolytic cells are required. The requirement of manpower is dramatically lowered from the present 1,12 hours/ton Pb of San Gavino to 0,8 hours/ton Pb cast into ingots.

### Electrolytic and thermal refining

124. Referring to a plant treating 50,000 tons/year of bullion of composition: Cu = 1,7% ; Sb = 1% ; As = 0,1% ; Bi = 0,00% ; Ag = 0,07% , a comparison between thermal and electrolytic refining is given roughly as follows:

#### Flow-Sheet

##### Thermal Treatment

##### Electrolytic treatment

- |  |  |
|--|--|
| 1. Dressing by cooling and stirring                  | 1. Dressing by cooling and stirring                        |
| 2. Deslagging by sulphur addition                    | 2. Anode coating   |
| 3. Arsenic removal by sodium hydrosulfide            | 3. Electrolytic refining in the cells                      |
| 4. Antimony removal in kettle by air                 | 4. Cathode coating   |
| 5. Desilverization by Parkes process                 | 5. Additional treatment with H <sub>2</sub> O <sub>2</sub> |
| 6. Desliming by vacuum distillation                  | 6. Copper trace treatment in short rotary furnace.         |
| 7. Additional treatment with NaOH                    | 7. Slime treatment:  |
| 8. Antimony desliming by Small-Bottomer process      | a) Melting in short rotary furnace                         |
| 9. Final refining with sloping bed                   | b) Slowing in converter                                    |
| 10. Further NaOH treatment                           | c) Separation in Cupel furnace for Silver recovery         |
| 11. Copper trace treatment in short rotary furnace.  | d) Recovery of Slimes                                      |
| 12. Arsenic trace treatment in short rotary furnace  |  |
| 13. Antimony trace treatment in short rotary furnace |  |
| 14. Smelting up of Slime Slimes:                     |  |
| a) Smelting in cells                                 |  |
| b) Zinc distillation in Parkes & Reed furnace        |  |
| c) Separation in Cupel furnace for Silver recovery   |  |
| 15. Smelting up of Slime Slimes.                     |  |

125. Comparable review of basic equipment - Although two completely different treatments are in concern, comparison of equipment shows that there are, nevertheless, some equal or similar equipments.

126. Dressing and removal of copper, in both treatments it is effected in 1 or 2 separated kettles with fire hearts.

127. To the complete equipment of electrolysis with departments for anode casting, electrolyte preparation, mud filtering and cathode melting as well as lead casting, corresponds in thermal refinery complete equipment for softening, Cu removal, Zn removal, Bismuth removal and final refining of lead to be casted into ingots.

128. To the equipment of anode mud processing and copper dross processing in electrolytic refinery, corresponds the equipment for by-product processing in the thermal refining.

129. For copper dross processing, fire (flame) furnaces or short rotary furnaces are envisaged for both treatments.

130. For anode mud processing in the electrolytic treatment the following basic equipment is scheduled:

- 1 each short rotary furnace
- 1 each converter
- 1 each cupellation furnace
- 5 each small kettles for % refining

130 b. Processing of by-products in the thermal treatment is envisaged by the following equipment:

- 2 each furnaces Baker du Four
- 1 each cupellation furnace
- 1 each short drum type furnace
- 1 each kettle Baker Hill for Bi-eling processing

Comparison and quality of products

131. Both processes should produce the same product. Only still be slightly different in their composition:

Product	Composition	
	Thermal refining	Electrolytic refining
<u>Refined lead</u>		
Pb	99.99 %	99.99 %
Cu		1.0 g/ton
As		trace
Bi		2.0 g/ton

0	100 g/ton	2-1 g/ton
0	-	2-1 g/ton
Lead lead	75 Pb 75 Sn	75 Pb 75 Sn
Lead-tin alloy	25 Sn 75 Pb 75	25-25 Sn 75-75 Pb
Sliver	Lead 75, 25 Ag	Lead 75, 25 Ag
Refined residue	75, 75 Sn	75, 75 Sn

12). It is noted that there is a difference in quality the refined lead. The electrolytic refining paper product is produced particularly as to its content.

**Lead and quality of by-products**

13). Lead and quality of by-products produced in the electrolytic refineries are considered, different. The notes show that quality of by-product in the electrolytic refining is considerably larger than the quality obtained in the electrolytic refining. Notes are shown lead and quantities of by-products for both refineries:

	<u>Electrolytic Refining</u>	<u>Electrolytic Refining</u>
	10,000 ton/p.	1,000 ton/p.
Copper losses		
Lead residue (lead paying and other treatment)	100	20
Antimony losses	20	
Arsenic losses	1,000	
Ag rich losses	1,000	
Legated losses (Pb - Ag - Sn)	100	
Ag rich lead	100	
Sliver	100	
Lead Sn losses (Pb, Sn)	2,000	
Sliver Sn losses (Pb Sn)	100	
Sliver residue	100	
Sn - Ag - Pb residue and sliver	100	
Final residue of tin		1,000 ton/p.
a) Pb - Sn - Ag alloy		100
b) Sliver Pb - Ag - Sn - Sn		100
c) Pb - Sn - Ag - Sn alloy		100
d) Final lead		100
	<hr/>	<hr/>
	10,000 ton/p.	1,000 ton/p.



16. The total amount of by-products in electrolytic refining is one third of that obtained in thermal refining.

17. Cost Recovery - Cost recovery in electrolytic process is slightly higher than in thermal process partly due to it that as a final product a refined lead containing less impurities is produced and partly due to it that there is less loss of the quantity of by-products in electrolytic process as largely smaller and the same process of electrolytic is effected at low temperature. The following figures for total recovery are generally accepted:

	<u>Electrolytic Ref.</u>	<u>Thermal Ref.</u>
75	77.1 %	75.0 %
80	75.0 %	75.0 %
85	75.0 %	75.0 %
90	75.0 %	75.0 %
95	75.0 %	75.0 %

18. Output of refined lead is larger in electrolytic refining due to the higher total recovery.

19. Labour Force - Labour force is used as a base for comparison:

<u>Electrolytic Refining</u>		<u>Thermal Refining</u>	
Operative department head	1	Operative department head	1
Foreman	2	Base Foreman	1
Working and waste sorting	6	Foreman	6
Working sheets	2	Refining	10
Replacement of anodes and cath.	6	Slime production	2
Slime filtering	1	Slime production	2
Waste sorting and light work	1	Short anode furnace	15
Logger down and waste slime processing	15	Crane operator	6
		Working benches	8
		Left hand	1
		Slime sorting	1
<b>Total</b>	<b>39</b>	<b>Total</b>	<b>57</b>

20. Labour force is almost two times in thermal process due to the higher amount of by-products to be treated.

21. Production Losses - The following figures are related to 1 ton. of refined lead:

	<u>Thermal ref.</u>	<u>Electrolytic ref.</u>
Lighter	kg. 1,2	"
Time	" 3,2	"
Cost	" 1,1	0,8
Waste	" 0,5	"
Ca	" 0,45	"
Ag	" 2,1	"
Slag	"	0,5
Smelting	"	0,5
Refining	"	2,5
Oil	" 40	20
Electric power	Kwh 25	140
Maintenance	n/1 1,1	0,6
Gas power	n/1 1,8	0,85
Water	m <sup>3</sup> /t 3,5	3

140. Investments - The following figures are estimated:

	<u>Thermal ref.</u>	<u>Electrolytic ref.</u>
Operating equipment	\$ 750.000	950.000
Building	at 2500	5.000
	\$ 250.000	400.000
Installation	\$ 100.000	150.000
	<u>\$ 1.100.000</u>	<u>1.500.000</u>

Electrolytic plant = \$ 1.500.000  
Thermal plant = \$ 1.100.000 = 1,36

141. Lead bound - The quantity of lead bound in electrolytic process is considerably higher than in thermal. Lead is bound in anodes, in cathodes, in electrolyte, in settles for an amount of about 1400 tons. In thermal refining, bound quantities of lead amount to about 500 tons, which represents about 30% of the quantity bound in electrolytic plant.

142. Quality and uniformity of operations - Electrolytic process provides for better uniformity of operation and superior quality of lead.

143. Flexibility of production - Thermal refining may be advantageous as purification of lead could be adjusted as required. For instance it is not necessary to remove bismuth from lead when there is the possibility to sell lead containing bismuth. But in electrolytic refining, debismuthising is made always in the same way, without additional cost, also when the bismuth content raises

at the highest level. The same applies for silver and other impurities. The increasing of the content of all the impurities does not mean an higher amount of by-product as in thermal refining.

144. Hygiene requirements - Electrolytic refining provides for better hygienic and sanitary requirements. The content of lead in the ambiente of the cell room is currently less than 0,015 µg/mc.

145. Summarising, the advantages of electrolytic refining are:

- a) Higher recovery of lead, silver and bismuth
- b) Lower consumption of reagents, fuel and other materials
- c) Half the manpower used in thermal refining
- d) Better quality of refined lead
- e) Possibility to treat bullion containing whichever amount of impurities, without any increase in the operational costs.
- f) Better hygienic and sanitary conditions
- g) Wider market outlets for the lead produced.

146. Disadvantages, on the other side, are: investment costs 1,35 times higher than for thermal process, and higher lead bound.

147. The electrolytic lead refineries, largely mechanized and automated in several sectors, show good operating economics. Based on 15 years experience, electrolytic refining is not only completely satisfactory, but is also superior to any alternate procedure.

#### ACKNOWLEDGMENTS

The author acknowledges with thanks permission to publish this paper granted by Comm. Fulvio Costoro, managing Director of Montepi & Montevocchio. Thanks are also due to the Montepi & Montevocchio staff at San Gavino for the valuable assistance given.

Dr. Elia Fronti

Milan, 10th February 1969



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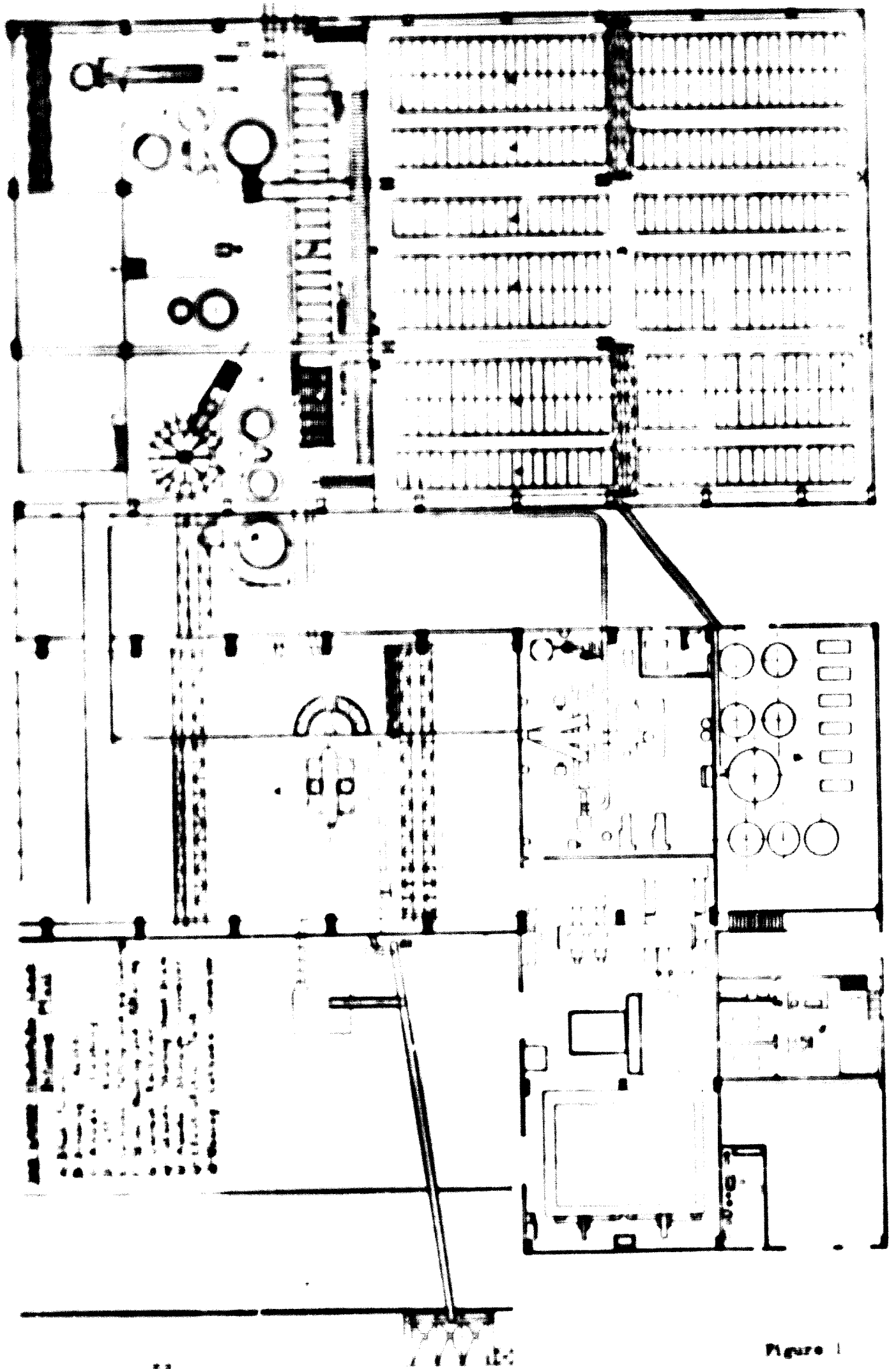
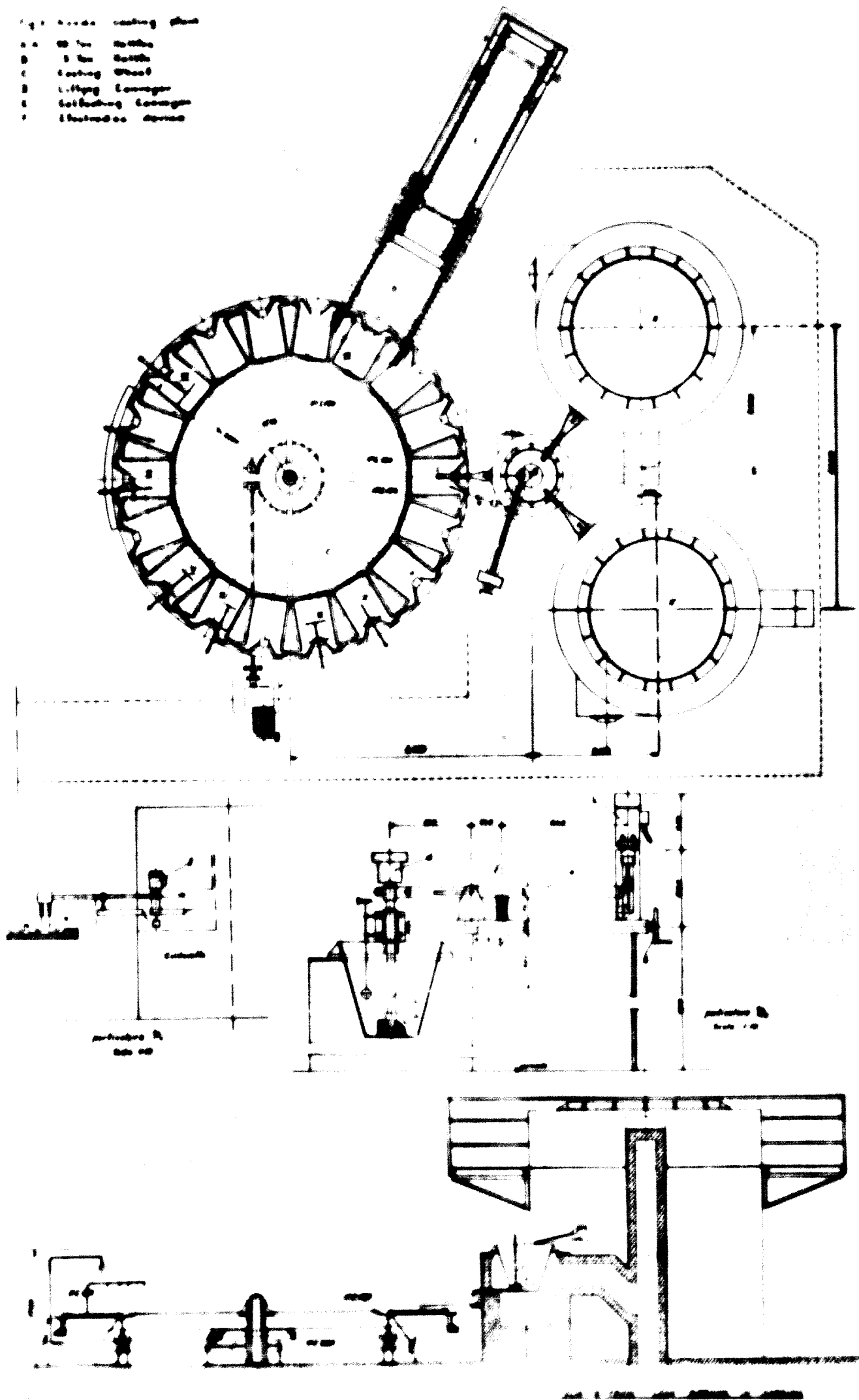


Fig. 1. Acacia casting plant

- 1. 10 ton bottle
- 2. 5 ton bottle
- 3. Casting wheel
- 4. Lifting conveyor
- 5. Collecting conveyor
- 6. Electrode device



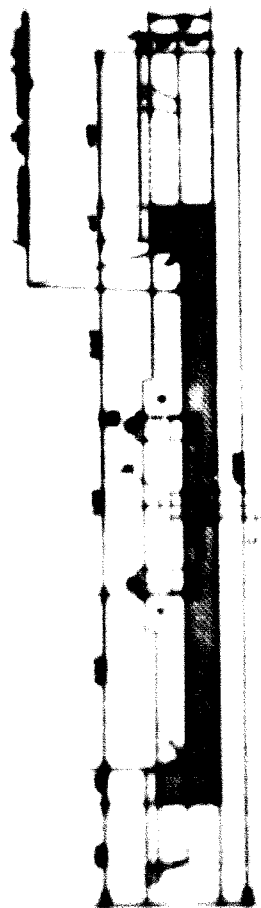
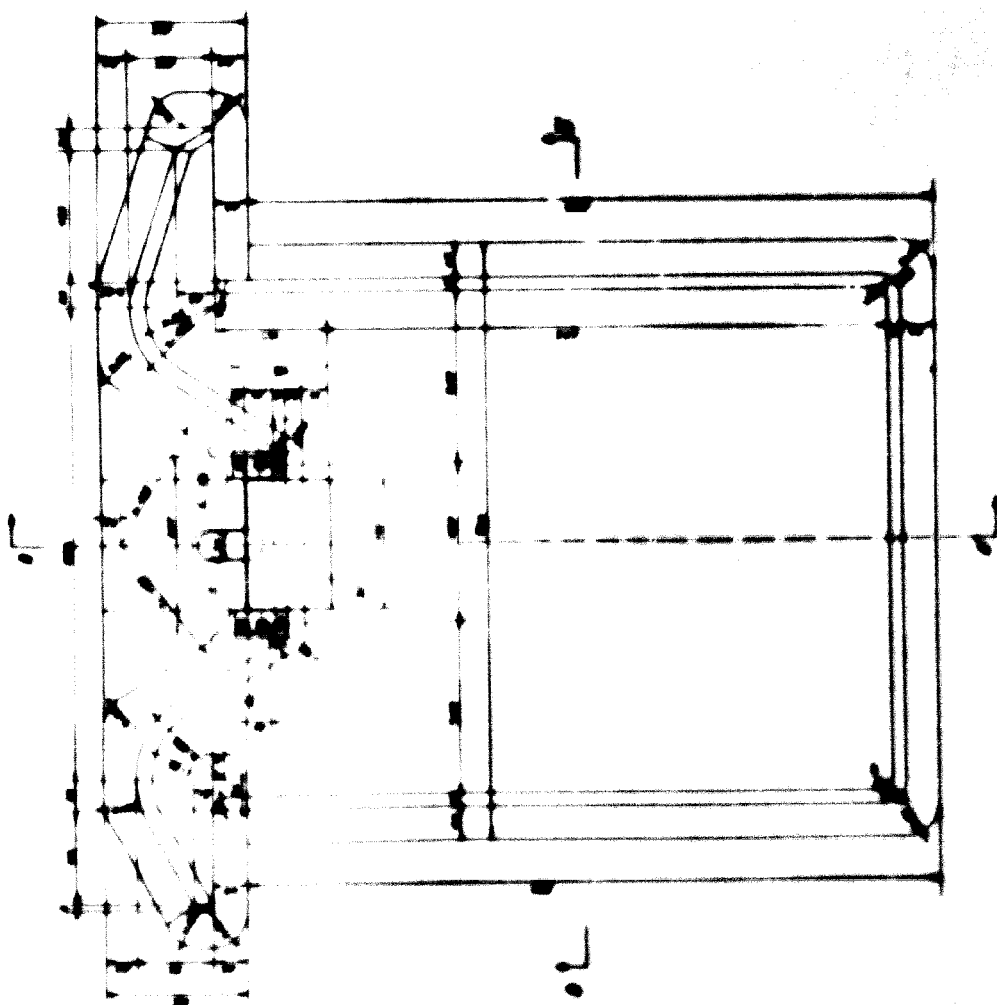
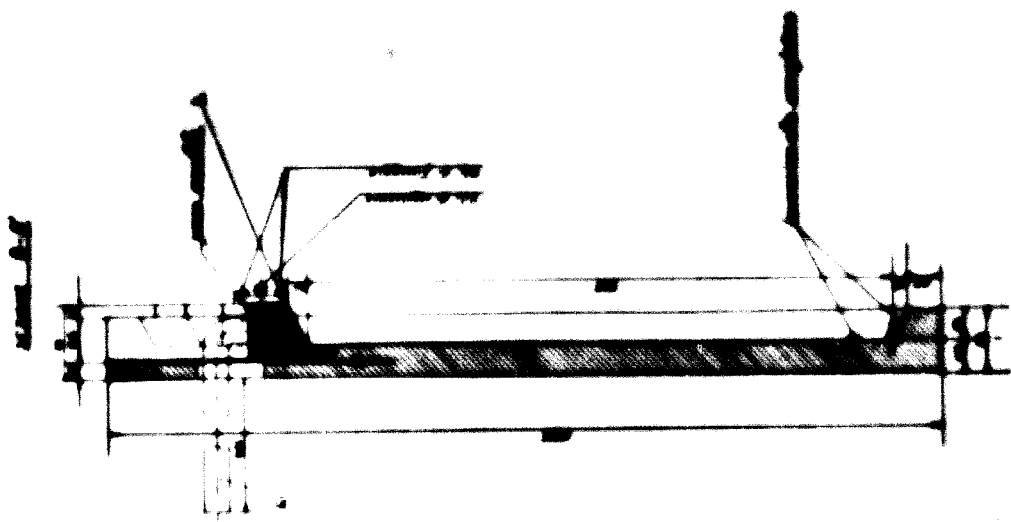
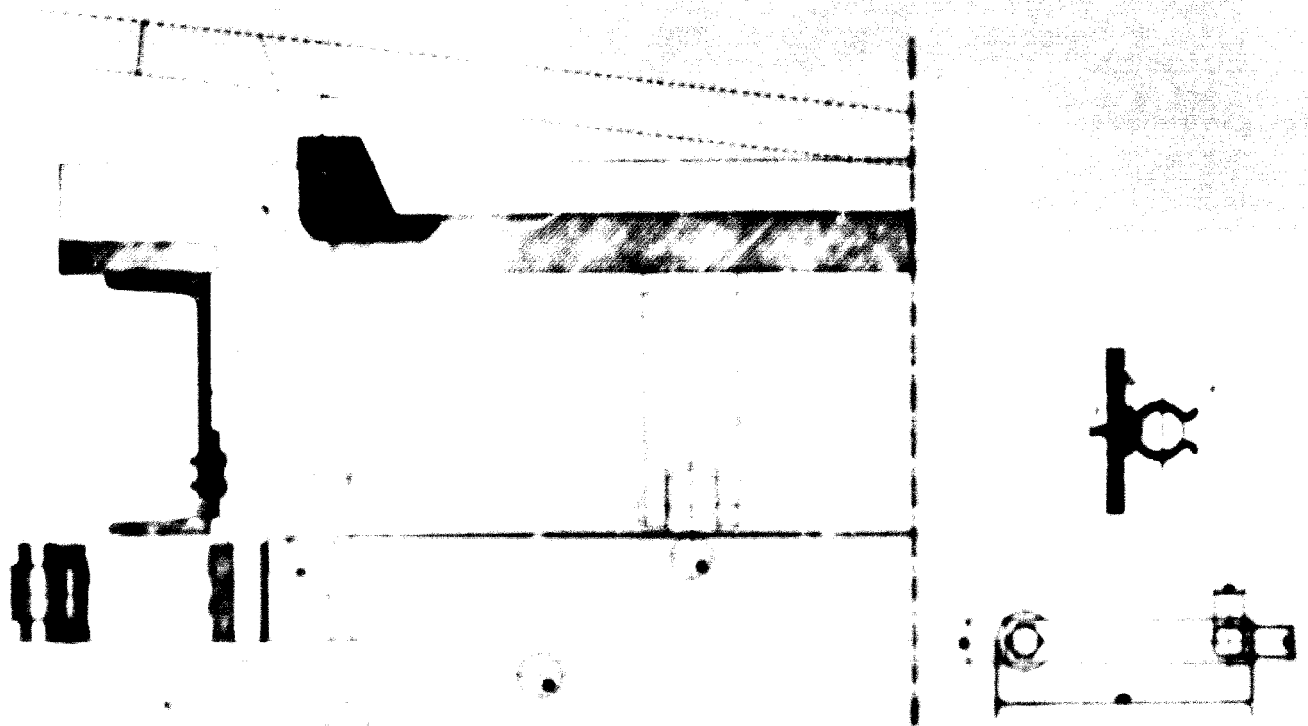
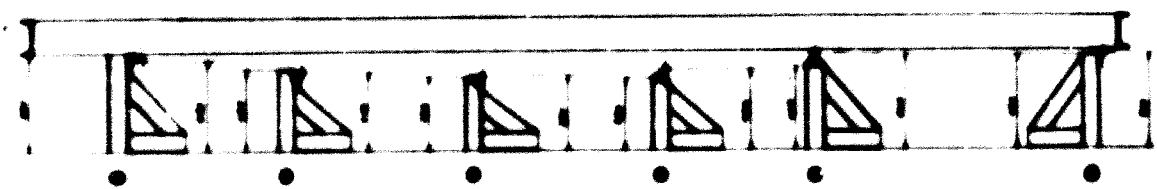
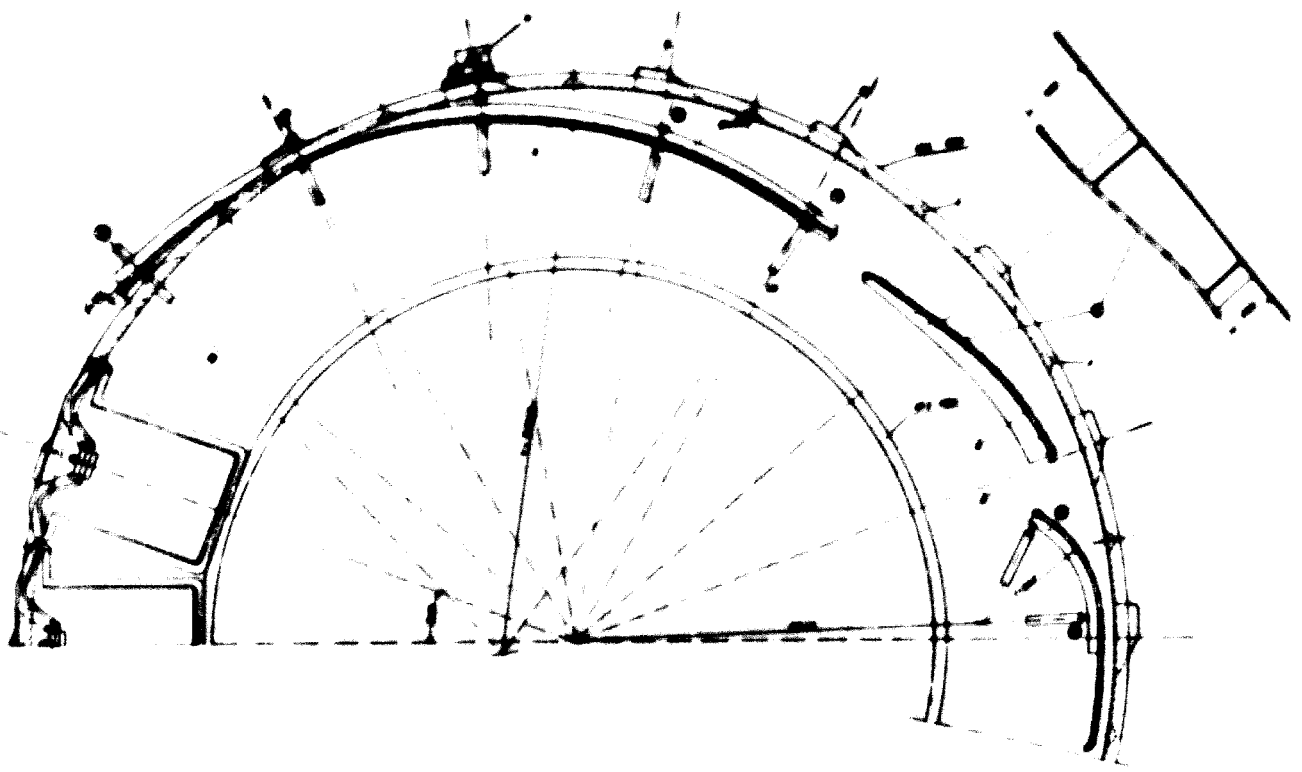


Fig. 8. - Valve, No. 10.

1000



Detail of roofing steel



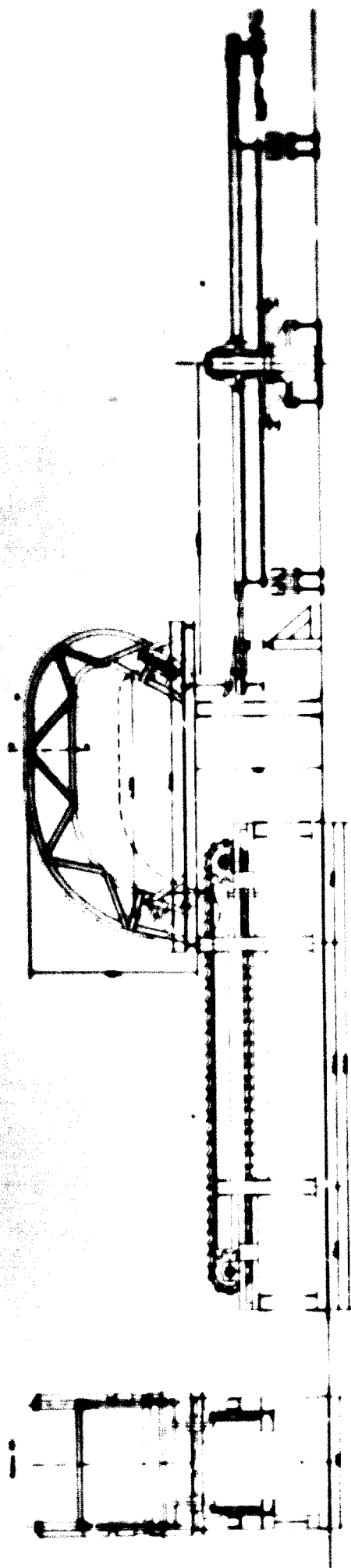


Fig. 5. — A detailed view of the curved mechanism shown in the main drawing.

Figure 5

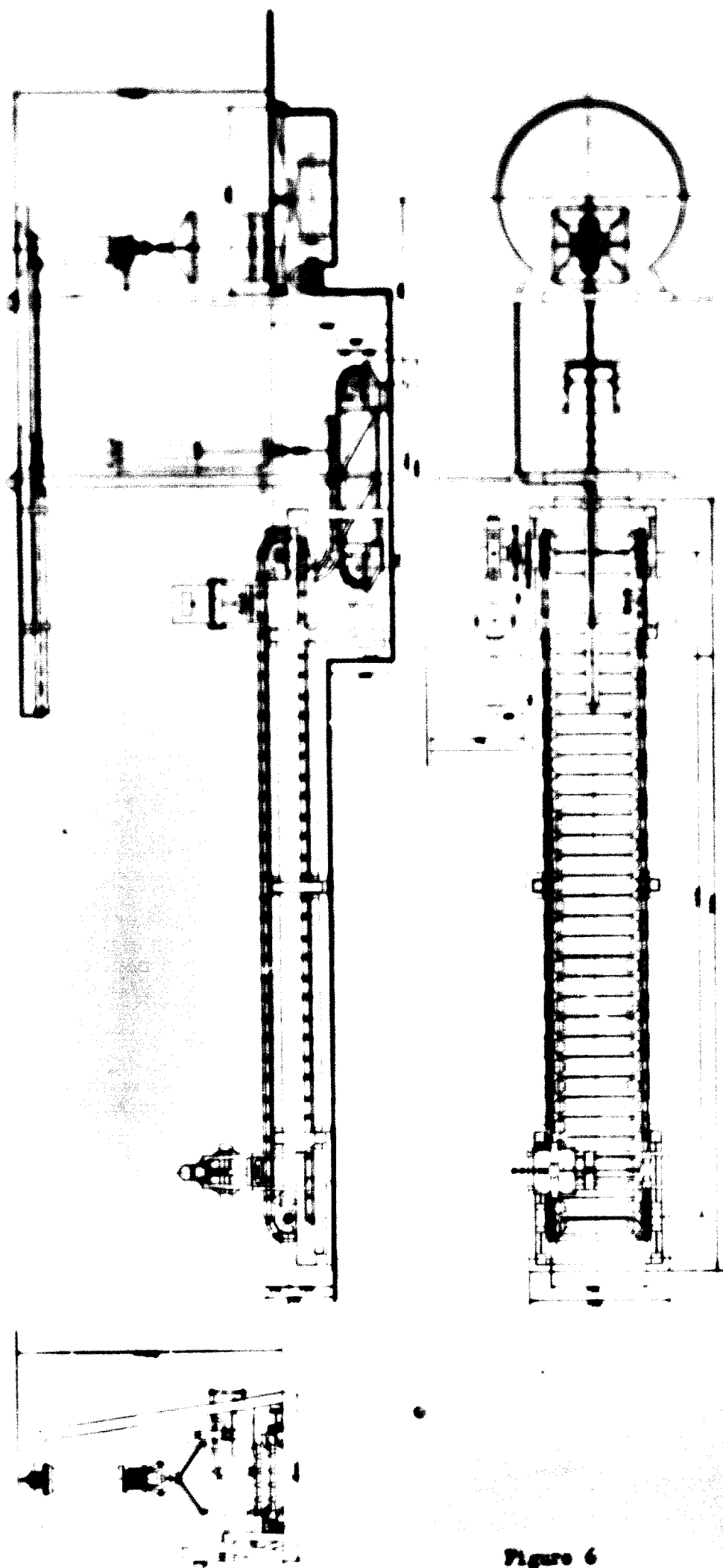
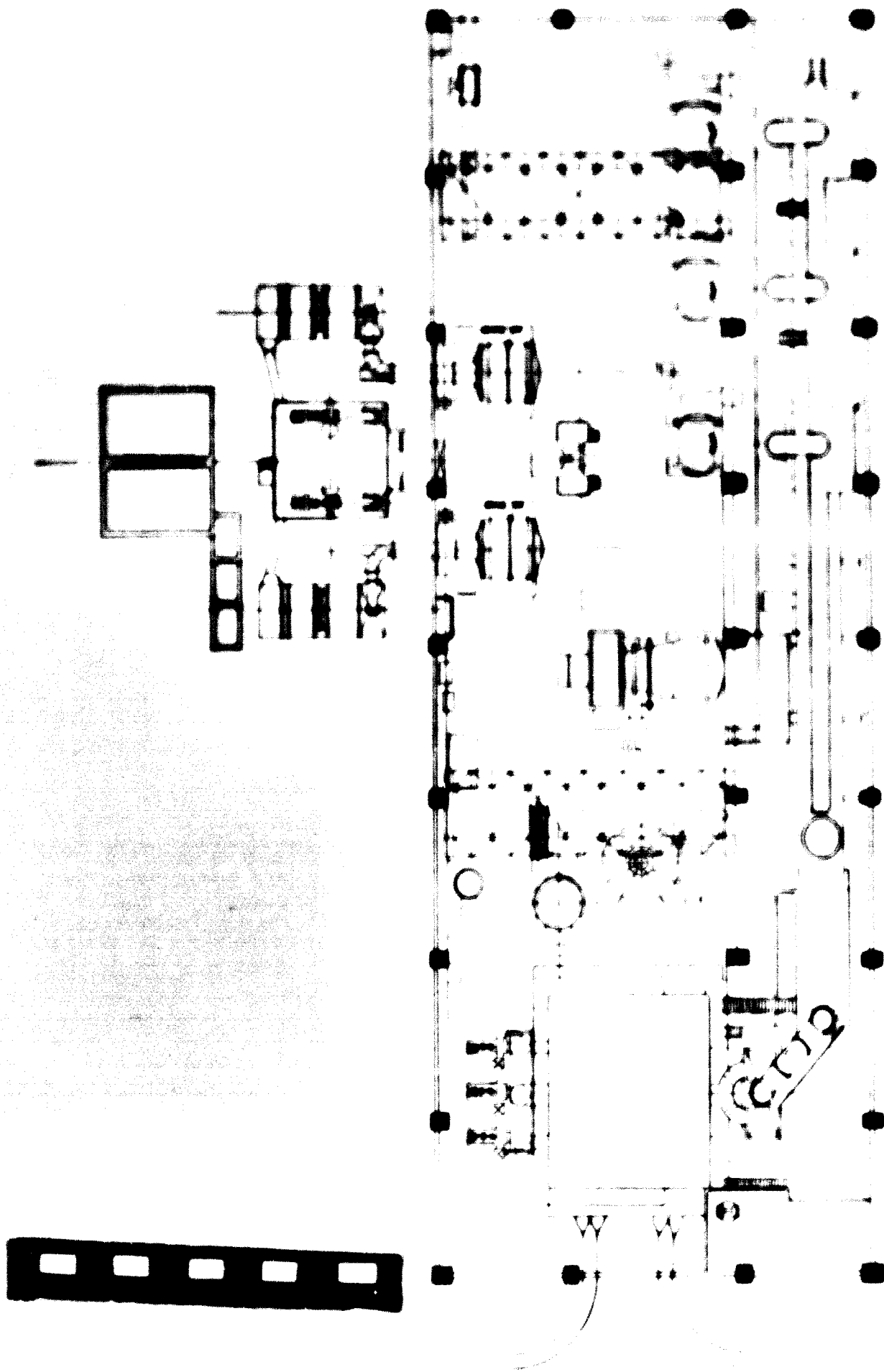


Fig. 6 - The Lead Pig, casting machine

Figure 6



Slime treatment plant

Figure 7

SLIME TREATMENT PLANT - LEAD REFINING IN SABINA



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