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LEAD AND ZINC REFINING AND TRENDS  
TOWARDS PURER METALS <sup>1/</sup>

by

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## INTRODUCTION

Until World War II the purity of the most standard metals was less than 99.9 per cent. A few metals reaching 99.99 % purity were produced in negligible quantities. The metal purity was determined by subtraction of the summary content of 5-10 limited contaminants from 100 per cent.

2. Nowadays, the technique of producing purer metals has greatly advanced. Creation of semiconductive devices, quantum amplifiers, microwaves and light radiation generators, superconducting materials, nuclear reactors, rocket and jet engines is impossible without metals of special purity, including lead and zinc.

3. Today, processes for production of many metals, including lead and zinc, with the summary content of impurities  $1 \cdot 10^{-2}$  to  $1 \cdot 10^{-7}$  per cent and often with the limiting content of 20-30 and more elements have been developed and mastered.

4. Depending on the field of application, metals are divided into three groups: metals of commercial purity, used generally for structural materials; pure metals, used in electrotechnics and high pure metals, used in new branches of technics.

5. Lead and zinc are those metals, which are used in all three groups.

6. Lead of commercial purity is used for making accumulators, cables, rolled metal goods, white lead, for ethylating benzene, for brazing and so on. Zinc is used for zinc plating, for brass and bronze production, for production of zinc white and for other purposes.

## I . L E A D

### I. LEAD SMELTING PROCESSES. DEPENDENCE OF LEAD PURITY ON THE COMPOSITION OF RAW MATERIALS AND PROCESSING TECHNIQUES

13. The purity grade of lead and zinc is determined by the composition of raw materials and processing techniques. Blast smelting of a sintered charge is the main lead smelting process. This process yields about 85 per cent of world's lead output. <sup>I</sup>

14. For the recent years, blast-furnace smelting process has been greatly improved due to oxygen enriched blast, which was first realized on a commercial scale in the USSR and in Canada.

15. In addition to blast-furnace smelting, the following processes are used for lead concentrate treatment :

a) Smelting by ore-hearth process. This kind of smelting is employed at those plants, which have in their disposal very rich (more than 70 % Pb) and pure, as to impurities (copper, zinc) lead concentrates.

b) Reactor smelting in short-drum rotary furnaces.

c) Electrosmelting of sinter. It is only employed at Ronshor smelter (Sweden).

16. In the USSR on pilot-plants, an entirely new process of lead-zinc concentrate smelting is being developed, the heart of which is flash smelting of these concentrates in an atmosphere of oxygen with a further additional treatment of the melt in an electric-furnace of the assembly, yielding fluid zinc and lead.

17. The composition of lead bullion /weribilei/ depends on the impurities content in a charge and fluctuates in a great extent. Usually, metal content in lead bullion equals 95-98 per cent.

### 2. LEAD BULLION REFINING PROCESSES

18. Commercial lead purity is determined by the processes of bullion refining.

7. Pure lead is applied for making some special kinds of accumulators and pure zinc - for making silver-zinc accumulators and special alloys for pressure casting.
  8. Lead and zinc of high purity find their application in atomic field, in the production of luminophores and semi-conductors.
  9. The general trend is seen in ever increasing demands for purer lead and zinc even in those branches of industry, which formerly have been satisfied with less pure metals (for instance, engineering, motor-car industry, etc.). This makes metallurgists continuously improve processes of producing purer metals.
  10. Today, the movement for metals purity has become an inseparable part of the technical progress.
- II. High pure metals permit to carry out researches in the field of fundamental sciences, signifying a new stage in the development of science that can lead to a revolution in technics.
12. Since the metal purity is determined by the technology of their production and by refining processes, these problems will receive special attention in this report.

19. The process of refining lead from impurities is of a great importance both for getting high-grade lead and for lowering losses of lead and other values in metallurgical processing.

20. The greatest metal losses at the stage of lead refining take place when lead is purified from copper and from noble metals including dross and silver foam treatment.

21. Lead bullion refining is usually accomplished with pyromethods with the consecutive removal of the following impurities: copper, arsenic, tin, stibium, noble metals, zinc, bismuth, magnesium, calcium. After copper drossing with a pyromethod, lead can also be refined by electrolysis.

22. For the recent years some refining processes were improved, many cleaning operations are accomplished with a continuous scheme (copper drossing, softening, desilvering, dezincing, debismuthing),

23. a) Copper drossing. Lead bullion copper drossing is the first stage of refining and almost at all the plants it is realized according to the standard scheme: rough segregation copper drossing with getting rich copper drosses and finally with sulphur.

24. While purifying lead from copper with a segregation method in kettles, about 12 % of lead, up to 50 % of silver, up to 65 % of gold, up to 60 % of stibium and more than 30 % of arsenic from the content of these metals in lead bullion are transferred to drosses, the gain of which equals 10-20 %.

25. Drosses are processed differently. At some smelters they are conveyed to a sinter charge, at others they are smelted together with other returns in blast furnaces. The most practiced method is dross smelting with flux, added in reverberatory furnaces.

26. All these processes especially above mentioned two lead to a great accumulation of metals in the products of lead production, as a significant part of copper and other metals, while dross smelting, transfer to the lead bullion and then again return to drosses. As a result of a continuous circulation of



Impurities, passing into drosses, gold, silver, copper, antimony and arsenic concentrate during the production circuit 2-4 times more, compared to the initial content of these metals in raw material. This increases metal losses, reagent consumption, lowers the efficiency of the main metallurgical equipment utilization and so on.

27. b) Lead softening (removal of As, Sb, and Sn). Lead softening is done with oxidizing and leaching methods. Oxidizing method of softening is realized in reverberatory furnaces, generally according to a batch scheme. Impurities are oxidized with air blown into the bath through submerged steel tubes. The practice of the Port Pirie smelter is a characteristic example of oxidizing lead softening according to a continuous scheme. With the continuous softening by oxidation, production is increased, the consumption of fuel and manual labour are decreased.

28. In some countries alkaline method of softening, yielding "dry" melts is practised. In the USSR refining methods with getting fluid melts are employed. This process advantages, compared to the oxidizing method, in getting alkaline melts, which contain negligible quantities of lead (1-5 %); it proceeds at a low temperature (400-450° C) and 4-5 times faster.

29. After softening the content of arsenic and antimony in lead fluctuates in the range of: As- 0.01 % - "traces", Sb - 0.1 - 0.025 %.

30. c) Desilvering of lead. At all the smelters desilvering of lead is accomplished with zinc. This operation proceeds with intervals in common vessels and at some smelters continuously in special vessels (Port Pirie, Australia and others)

31. d) Dezincing of lead. Dezincing of lead at smelters is done by different methods: alkaline, vacuum, oxidizing and chloridizing. In the USSR and in some other countries the alkaline method is employed.

32. At Port Pirie the process of continuous vacuum dezincing in a special apparatus is practised.

35. The oxidizing desincing in reverberatory furnaces is used at the works Bunker-Hill (USA) and Friedrich August (DDR). Desincing with chlorine gas is practised at the Braubach (DDR) and Trepcza works (Yugoslavia). The process proceeds at the temperature of about 300-400° C. After desincing, the lead contains from 0.03 to 0.3 % of zinc.

36. c) Debismuthing. The generally used method for bismuth removal is a calcium-magnesium method. For achieving better debismuthing they add stibium at some smelters. Magnesium is introduced directly into the vessel and calcium is added as a ligament with lead. Using this method the content of bismuth in the lead is lowered to 0.01 - 0.007 %.

37. In the Soviet Union a continuous process for debismuthing of lead with calcium and magnesium is developed.<sup>1</sup>

38. The process for debismuthing of lead with potassium and magnesium, which was developed and mastered at the Mulcaud-Godo smelter (France) is of an interest.<sup>1</sup>

39. 1) Final refining. Final refining of lead at all the smelters is accomplished with sodium hydroxide in common vessels, this is a batch process. The refining operation been completed, the smelters yield lead with 99.996-99.999 % content of the main metal that corresponds to the "CO" trade mark of the USSR's standard.

36. At some producers the electrolytic refining of lead is employed. Previously dressed and, in the case of tin presence and more than 0.3 % arsenicum, softened lead is delivered to the electrolysis.

37. Cathode lead, produced by an electrolysis, after washing is remelted in common refining vessels and is purified additionally out of the remained stibium, tin and arsenic with a pyro-method.

38. The electrolytic refining of lead is practised at the works of Trail, East-Chicago (USA), Oroja (Peru) and San-Cavino (Italy), Harima, Canto, Takekory, Saganocoky (Japan).<sup>1,2</sup> A solution of hydrofluosilicic acid serves as electrolyte, until 1935 a sulphamic acid electrolyte was used at San-Cavino.

### 3. SOME NEW PROCESSES OF LEAD REFINING AND TREATMENT OF THEREBY PRODUCED INTERMEDIATE PRODUCTS

#### a) Continuous copper dressing of lead bullion in an electric furnace.

39. Since 1956 in the Soviet Union researches are being conducted in laboratories and on a commercial scale for improving the process of copper dressing of lead bullion, they are fulfilled in two directions: 1) to transfer copper at the stage of dressing directly into the matte and 2) to realize dress treatment in an electric furnace.

40. The main features of both methods is the application of a furnace with a deep lead bath, having a temperature drop across the upper layers of about  $1000^{\circ}\text{C}$  and at the bottom of about  $400^{\circ}\text{C}$ .

41. At present, copper dressing, converting copper directly into the matte, is fulfilled at one of the smelters of the USSR in an electric furnace and at the other smelter it is realized in a furnace with a flame heating. Dressed lead is tapped out of the furnace continuously through a siphon, the sampling orifice of which locates at the level of the furnace bottom.

42. Lead concentrate and negligible quantities of soda are used as reactants. Sodium sulphide, formed thereby, lowers the temperature of the matte smelting and the lead content in it

43. Copper dressing in an electric furnace has the following advantages: the remained copper content in lead is lower, gas evolution is decreased, the temperature control is more accurate and the labour conditions are better.

44. Copper content in the dressed lead is 0.1-0.4%. The process is registered by the inventor's certificate of the USSR No. 120326 with the priority date from 21.III.1956. Later the process of copper dressing was modified as to design at Port Pirie by installing a special arrangement for cooling lead outside the furnace that enabled to raise the degree of lead purification from copper.

45. Lead content in the matte produced by dressing is somewhat higher. For lead removal, the matte is handled with soda in short-draw rotary furnaces (Port Pirie) or in a small reverberatory furnace (USSR).

## b) Agrossmilling of drosses

46. Another direction - dross handling in an electric furnace with a deep lead bath - does not exclude the drossing operation, but as not all the lead bullion is transferred to the electric furnace but only drosses, the furnace sizes are greatly reduced.

47. The availability of a deep lead bath makes possible to produce sufficiently pure lead and consequently to eliminate the recirculation of metals, taking place when drosses are handled with other methods. The method is registered by the inventor's certificate of the USSR No. 183 396 with the priority from 16.VI.1961.<sup>4</sup>

48. The process requires the addition of sodium sulphate and a reducing agent. Copper content in the matte is about 45-50% and lead content is about 5-7%. Copper converting into matte reaches 96%. Noble metals and stibium are converted into lead.

49. For theoretical bases of the processes said above, many of their features, including sodium-sulphide systems ( $\text{Cu}_2\text{S}-\text{Na}_2\text{S}$ ;  $\text{FeS}-\text{Na}_2\text{S}$ ;  $\text{ZnS}-\text{Na}_2\text{S}$ ;  $\text{Cu}_2\text{S}-\text{FeS}-\text{Na}_2\text{S}$ ;  $\text{Cu}_2\text{S}-\text{PbS}-\text{Na}_2\text{S}$ ;  $\text{FeS}-\text{PbS}-\text{Na}_2\text{S}$ ;  $\text{Cu}_2\text{S}-\text{PbS}-\text{FeS}-\text{Na}_2\text{S}$ ), characterizing copper-sodium matte, were studied.<sup>5-7</sup>

## c) Removal of arsenic from lead production dusts with a sulphatization method.

50. Many polymetallic ores contain essential quantities of arsenic. During ore beneficiation it contaminates lead, zinc and copper concentrates. Handling lead concentrates with a hydrometallurgical method, about 75% arsenic remains in lead residues which are treated in lead smelters. In the process of blast-furnace smelting about 60% of arsenic passes into sinter dusts and blast smelting fumes and about 20-30% of it is removed as calcium arsenate, while lead is refined with an alkaline melt.

51. Thus, lead production dusts represent an arsenic's collector. They contain from 30-40 to 100-200 kg of arsenic per ton of the dust. Dusts contain also in %: copper - 0.4-1; lead - 4-9; cadmium - 1-4; zinc - up to 20 and also some rare and scattered elements, i.e. these dusts are valuable raw material for metallurgical producers.

52. At the most smelters lead dusts are handled as returns in sintering. Dust return leads to recirculating, and accumulating, arsenic in products, thus complicating the technology of lead production and refining.

53. A method of treating lead dust with removal of arsenic out of the technological process and complex extraction of non-ferrous and rare metals has been developed in the Soviet Union. This method is registered by the inventor's certificate of the Soviet Union No. 105372 from 24.II.1956.<sup>8</sup>

54. The main feature of it is the granulation of dusts with strong sulphur acid on a disk granulator with a further thermic treatment of pellets in fluid-bed furnaces at a temperature of 350-380° C. Under these conditions more than 80 per cent of arsenic as well as selenium, chlorine and fluorine are extracted from dusts.<sup>9</sup> Non-ferrous and some rare elements are transferred into sulphate forms and are extracted into solutions, when a hydrometallurgical treatment of sulphatization products is used. The transference degree of main metals - zinc and cadmium - into water soluble forms equals 95-98%. The evolved arsenic is trapped in a wet gascleaning system and leaves as arsenite or calcium arsenate.

55. Arsenic removal by means of sulphatization of lead dust is 2 times cheaper, compared with its removal out of fluid alkaline melts after lead softening.

56. At the enterprises of the Soviet Union industrial divisions, dealing with the treatment of lead production dusts with the above mentioned method, are built and put into exploitation.

#### d) Electrothermics of silver foam

57. A modern technology of removing noble metals from silver foam, which is produced at the stage of lead bullion desilvering, almost at all the smelters comprises two stages: distillation of zinc from silver foam in vapor-du-baur retort and cupellation of silver lead, yielding a gold-silver alloy.

58. Treatment of silver foam in retorts has some essential disadvantages, the main of which are low productivity, low di-

direct recovery of precious metals into silver lead. Low recovery of zinc and arduous manual labour in harmful sanitary-hygienic conditions.

59. In 1956-1957 a new electrothermic technique of silver foam treatment was developed and examined on a semicommercial scale in the USSR.<sup>10</sup>

60. In 1957 mastering of a new electrothermic technique of treating silver foam, instead of the low productive retort method, carried out in Faber-du-Faur furnaces, was completed in the Soviet Union, for the first time in a world practice, on a scale of the whole branch of the lead industry.

61. The electrothermic technique of silver foam treatment is registered by the inventor's certificate of the USSR No. 59280 with the priority date from I.II.1957.<sup>11</sup>

62. The new technique of silver foam treatment is based on distilling zinc off into a gas foam with the following condensation of its vapour into liquid metal and converting noble metals into silver lead in pressure-tight electrothermic furnaces, in which an artificially prepared slag serves as a resistance body.

63. The electrothermic plant comprises an electric furnace, a liquid condenser, an inertial gas-trapper and a flue for driving gasses off into a bag-house. An ordinary coke is used as a reducing agent. Furnace charge with foam is mechanized and is accomplished continuously.

64. As a result of foam distillation in an electric furnace two products are produced: silver lead and metallic zinc, tapping of which through a siphon is accomplished from the electric furnace and the condenser respectively. The metallic zinc is used in copper dressing process of lead bullion and silver lead is conveyed to cupellation for noble metals extraction.

65. The process is characterized by the following technical-economical indices:

day's output of the plant is 4-5 tons of foam per sq.m of the electric furnace hearth area;

direct recovery of noble metals into silver lead is of about 100%, lead-99.5%, zinc into liquid metal-95%.

power consumption per t of foam equals 200-300 kwh/hr, consumption of electrodes - 5-10 kg, that of reducing agents (coke) - up to 20 kg.

66. Mastering the new method for silver foam treatment, in comparison with the retort process, made possible:

- to raise labour efficiency due to application of one electrothermal plant instead of several retorts;
- to mechanize the process;
- to raise the recovery of gold, silver and lead into silver lead and that of zinc into a compact metal.
- to eliminate dross formation and to exclude tedious operation for its treatment in cupel furnaces;
- to simplify a dust-collection system, owing to few gasses.
- to ensure normal sanitary-hygienic conditions that has completely excluded lead intoxication of a staff.

67. As the experience of mastering this new process has shown, the investments for building and erection of the electrothermal plant are compensated for one-three months.

#### 4. PRODUCTION OF HIGH PURE LEAD

68. Metals of high purity are produced in relatively negligible quantities and it is very difficult to differ their commercial production from research work.

69. Lead of high purity is used in apparatuses of atomic field and for production of semiconductor oxides ( $PbO$ ) and chalcogenides ( $PbS$ ,  $PbSe$ ,  $PbTe$ ). Such lead with the purity of 99.999-99.9999 % is produced by some firms, such as L. Light and Co. Ltd. (England), Hoboken (Belgium) and others. <sup>12</sup>

70. A new method of producing high pure lead is developed and mastered on a commercial scale in the USSR. It comprises multiple selective-blocked amalgam electrolysis with a further vacuum mercury extraction. <sup>13,14</sup> The method is registered by the inventor's certificate of the USSR No. 113616 with the priority date from 7.I.1957. The lead purity is 99.999-99.9999 %, analysed for 24 impurities.

7. In the USSR, lead is produced on a commercial scale by means of pyrometallurgical processes of lead refining. For getting metals of still higher purity, lead purification processes with crystallization have also been mastered. High pure lead is also produced with electrolytic refining processes. 99.995 per cent lead<sup>10</sup> is also produced on a commercial scale at Paderno-Dugnano plant (Italy), where electrolytic lead refining with sulphuric acid solutions as electrolytes is practised. In the USSR lead purer than 99.999 per cent was got with the similar electrolytes, using deep solution purification and diaphragm electrodes.

## II. Z I N C

### I. BASIC ZINC PRODUCTION PROCESSES : PYROMETALLURGICAL AND HYDROMETALLURGICAL ONES AND THEIR INFLUENCE UPON ZINC PURITY

72. Until 1915 zinc was produced only with a pyrometallurgical process, based on zinc distillation in horizontal retorts. Later, zinc production processes were realized in vertical retorts, in electric furnaces and by means of LOP.

73. Zinc produced with all the pyrometallurgical processes is considered to be of low grade and is used chiefly for zinc plating. For the recent years a trend is noticed towards raising the grade of pyrometallurgical zinc with the help of rectification. Higher requirements to metal purity for alloy production, rapid development of electrotechnics and a lower electric power cost favoured the development of hydrometallurgical process of zinc production, ensuring purer metal.

74. In 1955-1957 the contribution of different processes in the world's zinc output is as follows: hydrometallurgical-74%, distillation-32.5%, electrothermic-7%, LOP-6.5%.<sup>11</sup> In the USSR zinc production has been developed and will be developed further by a hydrometallurgical process, and also by an electrothermic process.

### 2. PRINCIPAL FACTORS INFLUENCING THE CHOICE OF ZINC PRODUCTION TECHNIQUE

75. Pyrometallurgical processes of zinc production were being constantly improved, especially since the thirties years of this century, and as a result of it they became continuous,



mechanized and highly productive. One of the technical achievements in pyrometallurgy of zinc was mastering by Imperial Smelting Corp. lead-zinc concentrates smelting in blast furnaces with zinc condensation into a liquid metal. Significant improvements in roasting, sintering and recalcification of zinc also favoured the development of the pyrometallurgical processes of zinc production.

76. Improvements of the hydrometallurgical processes of zinc production were marked with the application of roasting in a fluidized bed, improvements of calcine classification process, leaching, filtration, purification of solutions from impurities and zinc electrolysis.

77. Success of pyrometallurgical processes of zinc production, especially mastering electrothermics and blast-furnace smelting, made possible to process more complex and low-grade raw materials.

78. As the world practice shows, in some countries, especially where there are resources of cheap electric power, such as the USSR, the USA, Canada, Australia, Spain, Yugoslavia and some other countries, new hydrometallurgical zinc plants are being built and the functioning ones are being enlarged.

79. The problem of choice, whether pyro- or hydrometallurgical process should be used, depends upon many factors, namely upon raw material composition, upon availability of cheap electric power or coke, upon the fields of zinc application in a given country and upon a number of other reasons. Moreover, one should take into account that a hydrometallurgical process, as far as the raw material is concerned, is more "delicate", makes higher requirements to a concentrate grade and, as a rule, it is connected with greater investments. In the end, the both processes should be considered as perspective for further development and the problem of their use must be solved in each concrete case by means of careful technical and economical analysis.

### 3. PROCESSES OF PYROMETALLURGICAL ZINC REFINING

80. At present, this problem is given a great attention. Research is made in two directions: desincing by distillation and working out chemical methods of purification.

81. The content of impurities in metallic zinc produced by the electrothermic method reaches 5 per cent and more and is determined chiefly by the composition of an initial raw material. The refining of such zinc with a rectification method ensures the production of high pure metals, however, such refining entails considerable expenditure on power and some difficulties connected with equipment design for this process.

82. A segregation method of purification provides a partial improvement of zinc grade, as to lead and iron content. This method is based on the changes of solubility of metals -impurities or their compounds; the melt temperature been changed, the non-mixing phases, formed thereby, are separated by their specific gravity. The lead content in zinc always exceeds 1% after segregation refining.

83. Recently, a method of purifying zinc from impurities (lead, arsenic, tin, antimony, iron) by means of mixtures of alkaline and alkaline earth metals was proposed. The principal role is played here by such alkaline metals as sodium, potassium and lithium. The processing of zinc, having the lead content of about 1.2 per cent, with sodium metal reduces the lead content up to 0.5%. Reagent consumption is about 6.8 kg per 1 t. of zinc. The further reduction of lead content is achieved by vacuum distillation of zinc.<sup>13</sup> A pilot-plant for continuous vacuum deleading has been built on the suggestion of the Imperial Smelting Company and we hope that the representative of this company will be so kind as to tell us about it in detail.

#### 4. PURIFICATIONS OF SOLUTIONS FOR ZINC ELECTROLYSIS FROM IRON, COPPER, CADMIUM AND CHLORINE AS A NECESSARY CONDITION FOR PURE ZINC PRODUCTION

84. The purity of solutions, pumped for electrolysis, has a decisive meaning not only for the technical and economical indices of electrolysis, but determines also the produced metal grade. Of all the impurities, present in a neutral electrolyte, iron, copper, cadmium, cobalt and chlorine are of a greater importance for the zinc grade.

85. Iron. Iron, present in an electrolyte, discharges on the cathode together with zinc ions, forming two phases: zinc and a solid solution of iron in zinc.<sup>19</sup> For production of zinc, containing less than 0.003 per cent of iron, one should have not more than 1-2 mg per litre of iron in the solution. A hydrolytic method for purifying solutions from iron with its preliminary oxidation with manganese dioxide is practised at zinc smelters. When the hydrolytic purification of solutions from the dust cycle is done, the atmospheric oxygen, which under certain conditions serves as an active oxidizing agent, may find its application, such technique is widely used at the smelters of the Soviet Union. As a result of it, due to some improvements in pulp filtration and settling, the capacity of the division for leaching dusts and oxides has been slightly increased and the consumption of manganese ore has been decreased by 30-40 per cent.<sup>20,21</sup>

86. Copper and cadmium. Both of these impurities are more electropositive than zinc and, discharging at the maximum current, pollute the cathode metal. In order to produce zinc, containing less than 0.01 per cent of cadmium and 0.001 per cent of copper, a solution should not contain more than 4 mg/l of cadmium and 0.4 mg/l of copper. For producing purer zinc (0.002 per cent of cadmium, 0.0005 per cent of copper), the cadmium content in a solution must be lowered to 2 mg/l and that of copper - to 0.1 mg/l. Purification of solutions from copper and cadmium is carried out in the USSR by a continuous method, based on a counter-current principle.<sup>1</sup>

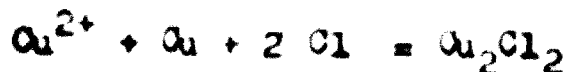
87. Cobalt. Cobalt does not pollute the cathode metal but it reduces amper efficiency. A xantogenate method for purifying solutions from cobalt has found its application in the USSR.<sup>22</sup> A new method of purification has also been worked out, the essence of which consists in simultaneous cementation of copper, cadmium and cobalt with zinc dust in the presence of an activating agent. Antimony salts are used as an activator. This method is registered by the inventor's certificate of the USSR, No. 117463, with the priority date from 9.11.1958.<sup>23</sup>

88. Works of other countries widely use purification of solutions from cobalt with  $\alpha$ -nitroso- $\beta$ -naphthol as well as cementation with zinc dust in the presence of arsenic salts.<sup>24</sup>

89. Chlorine. The presence of chlorine in an electrolyte increases corrosion of lead-silver anodes, rising the lead content in the cathode zinc. Researches in the Soviet Union have shown that by the chlorine content of about 200 mg/l, the corrosion of anodes equals about 250 g/t of zinc, when the chlorine content is increased up to 500 mg/l, the corrosion of anodes rises up to 600-1000 g/t of zinc. Furthermore, aluminium coils for cooling electrolytic tanks corrode quicker.

90. There is a number of methods for purifying solutions from chlorine. They are: washing oxides with hot water, precipitation of chlorine in the form of silver chloride with silver sulphate, precipitation of chlorine with mercurous sulphate, etc. The above mentioned methods have considerable shortcomings and do not give a desirable effect. The application of silver sulphate, though providing sufficiently good purification from chlorine, will entail a certain difficulty of silver regeneration, great losses and high cost of the latter, mercury salts are harmful for those who are engaged in them, while purifying there might be great losses of mercury and if entered the solution, it may cause serious disturbances of electrolysis.

91. A method of precipitation of chlorine from solutions in the form of a semi-chlorinated copper has got a wide application in the USSR. Copper cake of cadmium production, containing copper and zinc mostly in the form of fine metal powder, is used for this purpose. Precipitation of copper is based on the following reaction:



This method of purification is simpler and cheaper in comparison with other methods. However, the final chlorine content in the solution is not lower than 150-250 mg/l.<sup>1</sup>

92. While roasting oxides of wet-process and fumes, a part of chlorine is volatilized. But in this case the purification of solutions from chlorine is necessary as well, after it has accumulated in the solution.

93. In the USSR an extraction method of purifying zinc sulphate solutions from chlorine has been developed and examined on a

semicommercial scale. This method is registered by the inventor's certificate of the USSR and is patented in the USA, Austria and Belgium. A solution of a tertiary amine mixture ( $C_7-C_9$  fractions) in kerosene is used as an extracting agent. After extraction the chlorine content in solutions from leaching oxides of wet-process or fumes is reduced from 500-800 mg/l to 30-50 mg/l.

94. A partial dissolution of the extracting agent does not cause any objectionable consequences in zinc electrolysis, as the solutions of wet-oxide treatment, after purification from iron and arsenic, are transferred for calcine leaching.

#### 5. INFLUENCE OF THE ELECTROLYSIS RATE UPON THE ZINC GRADE

95. Most of zinc electrolytic refineries, including all the refineries built before World War II, operate by the current density up to 400 amp per square meter, only a few new refineries (Corpus-Christy, Valley field, Porto-Marghera and others) operate by the current density of 500 amp. per sq. m. and higher. All the refineries of the USSR employ the current density over 500 amp. per sq. m. (up to 650 amp. per sq. m.)

96. The increase of the current density reduces the content of impurities in the cathode zinc, discharging at the maximum current (copper, cadmium, iron), but in this case corrosion of anodes and content of lead in the cathode zinc are increased.

97. The increase of zinc content in a neutral solution rises its viscosity and makes the refining from impurities difficult. The rising of the electrolyte temperature reduces the grade of the produced metal, as the impurities in this case precipitate on the cathode more actively.

98. Commercial electrolytic zinc contains 99.975 per cent of the basic metal. The content of the main impurities is as follows: cadmium-0.01 per cent, copper-0.001 per cent, lead-0.015 per cent, iron-0.007 per cent.

99. According to the publications, most of the zinc electrolytic refineries produce zinc of several grades, including pure zinc, containing 99.99 per cent of the basic metal, which corresponds to the "1B" trade mark of the USSR's standard.

The higher grade of zinc as to the lead content is attained by introducing certain additions into the zinc electrolyte. For example, the Oreja plant uses barium hydroxide as an addition, the plants of Monsanto and Valley Field use strontium carbonate for this purpose. The application of such additions does not require high expenditures and designing any installations and at the same time ensures the reduction of the lead content to 0.003 per cent. The standard of the USSR provides for higher zinc grade - "RB4", the production of which is mastered by the Soviet refineries. Zinc of the "RB4" trade mark has the most strict limitations as to copper, lead and iron, the content of each of them should not exceed  $1 \cdot 10^{-5}$  per cent.

## 6. METHODS OF HIGH PURE LEAD PRODUCTION

101. For production of high pure lead three methods are generally used: purification by distillation, zone recrystallization and electrolysis. In the USSR researches have been made on purification of the electrolytic zinc with 99.995-99.998 per cent of purity, using the method of vacuum distillation, three fractions were picked out: the light fraction, the middle (basic) fraction and the residue. The yield of the middle - the purest fraction - made 50 per cent, the purity of the produced zinc was 99.99995 per cent.<sup>25</sup>

102. The Physical-Technical Institute of the Academy of Sciences of the Soviet Union<sup>26</sup> has purified zinc by vacuum distillation. Its purity has reached 99.99997 per cent; the yield of such zinc amounted to 40 per cent of the charge weight. The zinc purity was controlled by the method of residual resistance.

103. An electrolytic method of zinc refining has been worked out in the USSR. Commercial electrolytic zinc is used as an anode. The anodes are placed into diaphragms made of an acid resistance fabric. An electrolyte is a circulating solution of zinc sulphate, which is purified from copper, cadmium, lead and tin by cementation on zinc cuttings. The deep purification of solutions from iron, cobalt, nickel, copper, arsenic,

antimony and other impurities is made by means of complexing agents with subsequent adsorption of insoluble complexes by the activated charcoal. The final hydrolytic purification of solutions is made by freshly prepared zinc hydroxide, oxidation of iron and antimony is carried out with perhydrool or oxygen. Electrolysis is preceded by the current density of 500-600 amp. per sq. meter. As a result of it, the metal of 99.9991-99.9995 per cent purity, determined by subtraction of 14 impurities from 100 per cent (Ag, Cu, Al, Cd, Sn, In, Te, Bi, Co, Ga, Pb, Mn, As, Sb) has been produced.

I04. In connection with ever increasing demands for metal purity, zinc, refined by the above mentioned method, was subjected to a further refining by distillation and crystallization methods and the metal with 99.9999-99.99999 per cent purity was produced.

I05. The following methods are used for determination of impurities content in high pure zinc: spectral, chemical-spectral, colorimetric, polarographic, mass-spectrometric and radioactive methods of analysis.

I06. At present, a combined scheme, including electrolytic refining, rectification and zone melting, is used for production of zinc with 99.99999-99.999999 per cent purity.

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I07. Production of metals with high grade of purity is a very difficult problem, but industrial demands for them dictate an incessant work for deepening purification, developing new productive methods, methods of control and storage of pure matters.

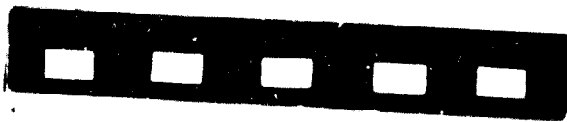
I08. Pure metals gain still newer and newer positions in science and industry, especially in the newest branches of techniques. Raising of metal purity leads to the deeper knowledge of a substance, revealing its concealed properties and consequently new spheres of use. Purity is an indispensable condition for bringing a hard substance structure to perfection and is a basis for creating materials with predicted properties.

R E F E R E N C E S

1. Abdeev, M.A., Getskin, L.S. et al. Modern processes of treatment of lead-zinc ores and concentrates. Moscow, 1964, 237 pp.
2. Nihon Kogyo Kaishi. J. Mining and Metallurg. Inst. Japan, 1967, 33, No. 955, pp. 1531-1541.
3. Novoselov, S.S., Bulletin' izobretenij i tovarnykh znakov, 1959, No. II, p. 37.
4. Polyv'annyi I.R., Bulletin' izobretenij i tovarnykh znakov, 1966, No. 13.
5. Novoselov, S.S., Kopylov, N.I., Sbornik trudov VNIITSVETMETa, 1962, No. 7.
6. Kopylov, N.I., Novoselov, S.S., Zhurnal neorganicheskoi khimii, 1964, vyp. 6, 8.
7. Polyv'annyi, I.R., Demcenko, P.O., Electrosmelting of copper drosses, Alma-Ata, Izdatel'stvo " Nauka ", 1967.
8. Getskin, L.S. et al., Bulletin' izobretenij, 1957, No. 2.
9. Getskin, L.S., Batjuk, A.G., Tzyt, P.P., Tsvetnye metally, 1957, No. 7.
10. Kershanskij, I.I., Tsvetnye metally, 1965, No. 2, p. 18.
11. Kershanskij, I.I., Bulletin' izobretenij i tovarnykh znakov, 1957, No. 10.
12. Werkstoffe für die Halbleitertechnik, prospectus of the Hoboken firm, Brüssel, 1964.
13. Ful'man, N.I., Bulletin' izobretenij i tovarnykh znakov, 1958, No. 6.
14. Ful'man, N.I. et al., Tsvetnye metally, 1966, No. 6, p. 39.
15. Sokolovskij, V.V. et al., Tsvetnye metally, 1964, No. 6.
16. Chemical Age, 1955, 7/II, 53, No. 1752, 251.
17. Metal Bulletin, 1965, No. 5127.
18. Woods, S., Temple, D., Bull. Inst. Min. and Met., No. 700; Transactions, 1964-1965, v. 74, No. 6, p. 297; express-inform., tsvetn. metallurg., 1965, No. 26.
19. Khan, O.A., Dukhanina, L.S., Zhurnal prikladnoi khimii, 1959, vyp. 4, pp. 823-826.



20. Getskin, L.S., Ponomarev, V.O., Tsvetnye metally, 1954, No. 1.
21. Getskin, L.S., Ponomarev, V.O., Zhurnal prikladnoi khimii, 1956, t. 29, vyp. 7, No. 7
22. Gromov, S.V., Pastukhov, A.I., Tsvetnye metally, 1946, No. 3
23. Klimenko, V.I., Method for purifying zinc solutions from cobalt., Bulletin' izobretenij, 1959, No. 2, p. 76.
24. Zelle, A., Kraiove Symp. Lastosow, Izotop. Techn., 3 rd, Stettin, Poland, 1956. (sect. 2); Chem. Abstracts, 1967, v. 66, No. 6, p. 2043.
25. Bregman, K.J., Grudinkina, M.P., Izmeritel'naij tehnika, 1961, No. 5, p. 23.
26. Alexandrov, B.M., Berlin, B.I., Fizika metallov i metallovedenie, 1960, No. 9, p. 362.





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