NEW TECHNOLOGY FOR LEAD

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Lead is an ancient metal, has been produced to-date from its ores exclusively by pyrometallurgical route.

The process suffers from numerous steps, high operating cost, and excessive pollution problems.
Galena
PbS
Metallurgy of lead

PbS concentrate

Air

Oxidation (sintering machine)

PbO

C

Reduction (blast furnace)

Solid-gas separation

SO₂

Ca, As

Solid-gas separation

To stock

Dust

Matte for Cu recovery

Settler

Speiss

Cooling, crushing, and grinding

Fuming furnace

Air

Slag

Zn

Lead bullion to refining
Refining of lead

1. Lead
2. Precipitation of impurities from melt (softening) → Impurities
3. Precipitation of silver → Pb–Ag
4. Selective oxidation (cupellation) → PbO
5. Refined lead
6. Silver
Refining of lead

Pb bullion from blast furnace

Cooling and
drossing ≈ 350 °C
(open kettle)

Cu–Pb dross

Elemental S

Sulfidation
(open kettle)

Cu₂S

Air

Oxidation 750 °C
(reverberatory furnace)

PbSnO₄

Air, Cl₂, or NaNO₃

Oxidation
(reverberatory furnace)

Slag contains
As and Sb

Ca

Removal of Bi

Dross

Softened Pb bullion
to desilverization
• The complex refining steps and the pollution in the neighborhood of smelters are causing much trouble to the nearby population.
• For example, the high content of lead in crab collected from the ocean in the vicinity of a lead smelter worries consumers.
• The appreciable amounts of lead in wine produced from a vineyard near a lead smelter causes concern to the industry.
• The maximum permissible limit for lead in the vicinity of a smelter is 0.05 mg Pb/m$^3$ of air or 6 ppb, a limit that is difficult to achieve in many plants.

• In addition, lead smelters produce SO$_2$ and this must be converted to sulfuric acid.

• A nearby market for the acid must exist. otherwise SO$_2$ will have to be emitted in the environment, which is unacceptable.
• As a result, a number of smelters and refineries have been shut down.
• Both problems can only be solved by using a hydrometallurgical route to process the sulfide concentrate.

• No lead fumes will be emitted in the environment and elemental sulfur could be produced, which is easy to store or ship to sulfuric acid manufacturers.
Hydrometallurgy of lead

• Extensive research has been going on since the beginning of the twentieth century to find a non-polluting process for its production and a solution for its complex refining scheme.

• It has been assumed correctly that the hydrometallurgical route should be the most promising.

• Pilot plants have been constructed and operated for a reasonable periods, but no process has proved to be fully satisfactory until recently.
First hydrometallurgical attempts

- O. C. Ralston US Bureau of Mines in Berkeley, California 1924 The solubility of PbCl$_2$ and PbSO$_4$ in brine solutions
Tainton at Bunker Hill in Kellogg, Idaho 1924

O₂ → PbS concentrate

Roasting → SO₂

H₂O → PbSO₄, impurities

Leaching

Filtration → Impurities

CaCl₂

Leaching

Filtration

PbCl₄²⁻ → Gangue, CaSO₄

Absorption

Cl₂

Aq. Electrolysis

Ca(OH)₂

Pb

Refining → Ag

Ag
Failure of Tainton Process

- Although it was supposed to be a sulfation roasting, yet some $\text{SO}_2$ was formed.
- In the electrowinning step chlorine was formed and was not disposed of properly beside its corrosion problems.
- Lead powder obtained was not satisfactorily handled and was contaminated by silver.

PbS Concentrate

O₂ → Aq. Oxidation → PbSO₄, Ag₂SO₄ → Filtration → CuSO₄, ZnSO₄ → Blast Furnace → CO₂, SO₂ → Refining → Crude Pb → Ag → Pb
Problems with Bunker Hill Process

• The process was thought to be more advantageous than the roasting process because no SO₂ would be evolved.
• In fact it was not, since SO₂ was generated in the blast furnace gases due to the decomposition of lead sulfate.
Other processes

Galena is attacked by dilute acids generating $\text{H}_2\text{S}$:

$$\text{PbS} + 2\text{H}^+ \rightarrow \text{Pb}^{2+} + \text{H}_2\text{S}$$

which can be collected and converted by standard technology to elemental sulfur at 400ºC using alumina as catalyst:

$$\text{H}_2\text{S} + \frac{1}{2}\text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}$$

However, the toxicity of $\text{H}_2\text{S}$ and its explosive nature renders this route undesirable.
Galena is attacked by concentrated $\text{H}_2\text{SO}_4$ at 100°C to form $\text{SO}_2$ and elemental sulfur:

$$\text{PbS} + 2\text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{SO}_2 + \text{S} + 2\text{H}_2\text{O}$$

The reaction is simple but offers no special advantage since $\text{SO}_2$ is generated.
Aqueous oxidation of PbS in acid

Aqueous oxidation of PbS in acid results in the formation of elemental sulfur:

\[
PbS + \frac{1}{2} O_2 + 2H^+ \rightarrow Pb^{2+} + S + H_2O
\]

- When \(H_2SO_4\) is used, \(PbSO_4\) will be formed and when \(HCl\) is used then \(PbCl_2\) will be formed together with an appreciable amount of \(PbSO_4\) since a portion of sulfide sulfur is oxidized to \(SO_4^{2-}\) and other components of the concentrate will form soluble sulfates.
Solution purification can be achieved by cementation of the impurities with lead powder. Ferrous ion can then be oxidized back to ferric for recyle. Oxidation may take place by oxygen:

\[ \text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O} \]

Or by chlorine when \( \text{FeCl}_3 \) is used:

\[ 2\text{Fe}^{2+} + \text{Cl}_2(\text{aq}) \rightarrow 2\text{Fe}^{3+} + 2\text{Cl}^- \]
There is no advantage in using the sulfate system because of the difficulties encountered in the recovery step. When Fe$^{3+}$ ion is used instead of oxygen the following reaction takes place:

$$\text{PbS} + 2\text{Fe}^{3+} \rightarrow \text{Pb}^{2+} + 2\text{Fe}^{2+} + \text{S}$$
Processing lead sulfide concentrates with formation of elemental sulfur. Chloride system
US Bureau of Mines Process in Reno, Nevada

• In this case chlorine could be obtained from the electrolysis of PbCl$_2$ either in aqueous solution (complexed with NaCl) or in the molten state.

• This was the basis of the processes developed by researchers at US Bureau of Mines and others.
• This shows again that the chloride system is more preferable than the sulfate system, since in the latter case the sulfate ion must be disposed of.

• Oxidation of Fe$^{2+}$ may also be achieved in the electrolytic step whereby the evolution of chlorine is suppressed as proposed by French researchers.
Carbonate system

To avoid the formation of PbSO$_4$ or PbCl$_2$, aqueous oxidation of PbS was conducted by Chinese researchers in presence of ammonium carbonate at about 50°C. Lead carbonate and elemental sulfur are formed:

\[
PbS + (NH_4)_2CO_3 + \frac{1}{2}O_2 + H_2O \rightarrow PbCO_3 + S + 2NH_4OH
\]

- Residence time about 6 hours and yield of sulfur is 60%. After flotation of elemental sulfur, PbCO$_3$ was solubilized in fluorosilicic acid, the solution purified, then electrolyzed for electrowinning of lead.
PbS concentrate

O₂

Aq. Oxidation

Filtration

Solids

Flotation

PbCO₃, gangue

Dissolution

H₂SiF₆

Recovery

(NH₄)₂CO₃

S, Ag

Residue containing Ag

Filtration

Purification

Impurities

Electrolysis

Pb
NITRATE SYSTEM

• The nitrate system has the advantage that both lead and silver will go into solution and hence separation can be readily achieved.

• Using HNO₃, however, has the disadvantage of generating nitric gases, which must be re-converted to HNO₃.
• The use of ferric nitrate was already proposed. the following reaction takes place:

\[ \text{PbS} + 2\text{Fe(NO}_3\text{)}_3 \rightarrow \text{Pb(NO}_3\text{)}_2 + 2\text{Fe(NO}_3\text{)}_2 + S \]

• Complete dissolution of galena took place at 70°C in 0.25 \( M \) \( \text{Fe(NO}_3\text{)}_3 \) solution at pH 1.2-1.4 in 100 minutes.

• While lead forms at the cathode, \( \text{PbO}_2 \) forms at the anode.
PbS concentrate

Regeneration

Dissolution

Leaching

Filtration

Solution

Bi, Cu, Ag, Zn

NO + NO₂

Heating

Solution

Fe₂O₃

Filtration

Purification

Electrolysis

Pb + PbO₂

Gangue

S
After purification of the solution from copper and bismuth by cementation on lead and the separation, if necessary, of zinc by organic solvents, lead can be recovered by electrowinning at the cathode as Pb and at the anode as PbO₂:

\[
Pb(NO_3)_2 + 2e^- \rightarrow Pb + 2NO_3^- \\
Pb(NO_3)_2 + 2H_2O + 2NO_3^- \rightarrow PbO_2 + 4HNO_3 + 2e^- \\
\]

Overall reaction

\[
2Pb(NO_3)_2 + 2H_2O \rightarrow Pb + PbO_2 + 4HNO_3 
\]
CHLORINATION

The use of gaseous chlorine has the advantage over the aqueous chloride system is the absence of PbSO$_4$ formation since all the sulfide sulfur is transformed to the elemental form.

There have been early attempts in this direction at the beginning of the twentieth century but without success owing to the difficulties encountered in handling chlorine.
About sixty years later, researchers at the US Bureau of Mines in Rolla, Missouri re-examined this technology and recommended the recovery of lead by the electrolysis of fused PbCl\(_2\).

A pilot plant was later operated at Hazen Research Center in Golden, Colorado based on such technology. Chlorine gas is fed to rotating reactor counter-current to the flow of fresh concentrate so that any sulfur monochloride formed becomes the chlorinating agent:
PbS + Cl₂ → PbCl₂ + S
2S + Cl₂ → S₂Cl₂
PbS + S₂Cl₂ → PbCl₂ + 3S

The temperature in the reactor is 155-175°C.
• Lead chloride and other chlorinated compounds are then solubilized in hot brine solution. Lead chloride is then crystallized and, the anhydrous PbCl₂ is fed in a fused salt cell containing 90% PbCl₂ and 10% NaCl and operating at 500°C.
• High purity lead was obtained.
• Mother liquor from crystallization step is treated with sponge iron to remove silver. A bleed stream is treated with NaOH or Na₂CO₃ to remove other impurities.
• Work at Universal Oil Products laboratory in Des Plaines, Illinois also confirmed this technology.
Since lead fluorosilicate is soluble in water, it was suggested by workers at US Bureau of Mines in Rolla, Missouri to leach lead sulfide concentrate in fluorosilicic acid:

\[
PbS + H_2SiF_6 + \frac{1}{2}O_2 \rightarrow PbSiF_6 + S + H_2O
\]
• After filtration of the residue and solution purification, lead can be recovered by electrolysis. The residue contained elemental sulfur, silver, zinc, and copper.

• Attempts to electrowin lead from the leach solution were not successful because of low current efficiency and undesirable cathode morphology due to impurities present.

• To overcome this problem, the Bureau of Mines researchers suggested adding H₂SO₄ to precipitate PbSO₄, transform the sulfate into carbonate, dissolving PbCO₃ in H₂SiF₆, then electrolyzing the pure lead fluorosilicate solution.

• High purity lead was obtained but the procedure suffers from the numerous steps involved and the generation of ammonium sulfate as a by-product.
PbS concentrate

$\text{H}_2\text{SiF}_6$

Leaching

$\text{O}_2$

Filtration

Solution

Purification

Electrolysis

Pb

Impurities

Flotation

Silver recovery

$\text{S}$
Researchers at Engitec Tehnologies in Milan, Italy found out that galena concentrates was solubilized in fluoroboric acid containing ferric fluoroborate at 80°C liberating elemental sulfur while silver, copper, bismuth, and antimony remain in the residue:

\[
PbS + 2Fe(BF_4)_3 \rightarrow Pb(BF_4)_2 + 2Fe(BF_4)_2 + S
\]
The solution is then electrolyzed in a diaphragm cell where pure compact lead is deposited at the cathode and the ferrous fluoroborate is oxidized at the anode to ferric fluoroborate for recycle:

- \( \text{Pb}^{2+} + 2e^- \rightarrow \text{Pb} \)
- \( \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \)
• After filtration of the residue and solution purification, lead can be recovered by electrolysis. The residue contained elemental sulfur, silver, zinc, and copper.

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PbS concentrate

\[ \text{HBF}_4 + \text{Fe(BF}_4)_3 \]

Leaching

Filtration

Solution

Electrolysis

Lead

Flotation

Silver recovery

S

Bleed for zinc recovery
• No oxygen is formed at the anode and this is a great advantage because the voltage will be lower.

• Air is sparged at the anodes to prevent the formation of PbO\textsubscript{2}.
• A typical electrolyte will have the following composition in g/L: Pb\(^{2+}\) 50-70, Fe\(^{2+}\) 25-30, Fe\(^{3+}\) 35-30, fluoroboric acid 35-45, total HBF\(_4\) 325-335.

• Temperature of electrolysis 35°C, anodic and cathodic current densities 200-250 A/m\(^2\), and graphite anodes can be used.

• Cell voltage at 300 A/m\(^2\) is 2.10 volts, the current efficiency is 96%, and energy consumption is 570 kWh/tonne Pb cathode.

• Lead produced is 99.99% and the overall recovery is 96.1%. Zinc is partially solubilized in the leaching step but not electrodeposited; it can be recovered from the bleed solution.
Fluoroboric acid

• Fluoroboric acid, HBF$_4$, is prepared industrially by reacting hydrofluoric acid with boric acid:

$$\text{H}_3\text{BO}_3 + 4\text{HF} \rightarrow \text{HBF}_4 + 3\text{H}_2\text{O}$$

• The reaction is exothermic and the acid is available only as a 48% solution.
• Ferric fluoroborate is prepared by reacting the acid with Fe$_2$O$_3$.
• Fluoroboric acid is more expensive than fluorosilicic acid but it has the advantage of being more stable on heating and its solutions have higher electrical conductivity.
• Fluoroboric acid was used for more than fifty year by Norddeutsche Affinerie in Germany for refining lead bullion with high bismuth content.
• Presently it is used in electrodeposition of lead and its alloys, especially in printed circuit board manufacture.
• Doe Run had a demonstration plant in southeast Missouri, running for more than 3 years. Now it is in stand-by.

• In the same location in Missouri there is a small unit (50 kg/d) that is available for testing.

• It is expected to invest more than $150 million.
Doe Run, Missouri
CONCLUSIONS

• Zinc had a similar history like lead up to 1980s. It was produced exclusively by roasting the sulfide concentrate to form zinc oxide, thermal reduction of the oxide, then refining the crude metal by vacuum distillation.

• During World War I, leaching of the oxide and electrowinning of zinc from the purified solution replaced the reduction and vacuum distillation steps.

• In 1980, the total hydrometallurgical route, i.e., aqueous oxidation of the sulfide concentrate to get zinc sulfate solution and elemental sulfur was introduced on industrial scale.

• Copper had also a similar history until at the beginning of the twenty first century when the aqueous oxidation of copper sulfide concentrates was also introduced on industrial scale by Phelps-Dodge in Arizona.
• Will lead follow a similar situation?
• The answer is yes.