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Chemistry of Lead:



Introduction:

The chemical symbol for lead, Pb, comes from the Latin word *plumbum*. This is where the word “plumber” comes from: in ancient Roman times, water pipes used in plumbing were made from this soft metal. Lead compounds are found in the minerals crocoite, anglesite, and galena – the main source of pure lead. Lead was used far more commonly in the past as an important ingredient in paints, hair-dyes, and insecticides. A common historical use was in glassware.

Occurrence:

The most important ore of lead is **galena or lead glance PbS** , which is widely distributed throughout the world. Other ore minerals of lead are:

- Anglesite (PbSO₄)
- Cerussite (PbCO₃)
- Pyromorphite (PbCl₂·3Pb₃(PO₄)₂) and
- Mimetesite (PbCl₂·3Pb₃(AsO₄)₂)

Other lesser minerals are Crocoite (or kollochrome, or red-lead ore) (PbCrO₄), Wulfenite (or molybdenum lead spar, or yellow lead ore) (PbMoO₄) and Stolzite (PbWO₄). **The main sources of lead** ores currently worked are in the U.S.A., Australia, Mexico, Canada and the U.S.S.R., but substantial quantities are mined in Peru, Morocco, Yugoslavia, Germany, Spain, South Africa, Italy and Bolivia.

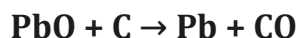
Extraction of Lead from Galena/Lead Glance (PbS):

Lead ores are initially crushed and concentrated by flotation, when lighter impurities such as zinc sulphide are removed. At this stage ore concentrates in general contain about 40 % of lead by weight.

Step I: The ore is roasted in air to convert the sulphide to oxide and sulphate, in which process extensive evolution of sulphur dioxide takes place.



Step II: Reduction of the resulting oxide (by coal/charcoal) to crude lead and SO₂ is converted into sulphuric acid.



Major impurities in the obtained crude lead are gold, silver, copper, antimony, arsenic and bismuth. At this stage the lead is hard, due to the arsenic and antimony present. The lead is now melted and kept molten at a temperature below the melting point of copper, whereby the copper present crystallizes and can be skimmed out. If air is now blown into the molten lead, arsenic and antimony float out as oxides, and after this process the lead is referred to as soft lead. Gold and silver may be removed from soft lead by the Parkes process. This involves the preferential extraction of silver and gold into added molten zinc, which then rises to the surface of the lead and after solidification can be skimmed off. The final impurity of a little zinc can be removed either by air oxidation, or more recently by evaporation.

This series of processes renders lead one of the purest of commercial metals, and the chemical specification for the purest commercial grade available in bulk requires 99.94% lead with no single impurity greater than 0.0025%, with the exception of bismuth which may be up to 0.05%. Lead may be further refined electrolytically up to 99.995%, and finally zone refining, produces lead better than 99.9999 % pure.

Note: In the earth's crust lead is estimated to be present as 1.6×10^{-3} % by weight, and to be in sea water at a concentration of 0.004 g/ton.

Physical Properties of Lead:

Lead has no allotropic modifications (atoms of the element are bonded together in a similar manner), and crystallizes with face-centred cubic structure ($a = 4.95$ Angstrom), with nearest neighbour lead-lead distance as 3.49 Angstrom. The outstanding physical properties of pure lead are its high density (11.3 g cm^{-3}), softness, malleability, flexibility, low melting point (327°C , low compared to other metals) low strength and low elastic limit. These characteristics, together with its high corrosion resistance, are the basis of most applications of lead metal.

Chemical Properties of Lead:

When freshly cut, lead oxidizes quickly, forming a dull gray coating, formerly thought to be lead suboxide, Pb_2O , but now recognized as a mixture of lead and lead monoxide, PbO , which protects the metal from further corrosion. Similarly, although lead is soluble in dilute nitric acid, it is only superficially attacked by hydrochloric or sulfuric acids because the insoluble chloride (PbCl_2) or sulfate (PbSO_4) coatings that are formed prevent continued reaction. Because of this general chemical resistance, considerable amounts of lead are used in roofing, as coverings for electric cables placed in the ground or underwater, and as linings for water pipes and conduits and structures for the transportation and processing of corrosive substances.

Elemental lead can also be oxidized to the Pb^{2+} ion by hydrogen ions, but the insolubility of most salts of Pb^{2+} makes lead resistant to attack by many acids. Oxidation under alkaline conditions is easier to effect and is favoured by the formation of the soluble species of lead in the +2 oxidation state. Lead oxide (PbO_2 , with lead as the Pb^{4+} ion) is among the stronger oxidizing agents in acidic solution, but it is comparatively weak in alkaline solution. The ease of oxidation of lead is enhanced by complex formation. The electrodeposition of lead is best affected from aqueous solutions containing lead hexafluorosilicate and hexafluorosilicic acid.

Applications/Uses of Lead:

Lead has many other applications, the largest of which is in the manufacture of storage batteries. It is used in ammunition (shot and bullets) and as a constituent of solder, type metal, bearing alloys, fusible alloys, and pewter. In heavy and industrial machinery, sheets and other parts made from lead compounds may be used to dampen noise and vibration. Because lead effectively absorbs electromagnetic radiation of short wavelengths, it is used as a protective shielding around nuclear reactors, particle accelerators, X-ray equipment, and containers used for transporting and storing radioactive materials. Together with the compound lead oxide (PbO_2) and with lead-antimony or lead-calcium alloys, it is employed in common storage batteries.

Lead Pigments:

Pigments are the substances which are used to give the proper colour to paints.

Types of Lead Pigments:

1. White lead Pigment:

- ❖ Chemical Name: Basic Lead Carbonate
- ❖ Chemical formula: $[\text{2PbCO}_3 \cdot \text{Pb(OH)}_2]$ or $\text{Pb}_3(\text{OH})_2(\text{CO}_3)_2$
- ❖ Used in white paints as a pigment. White color darkens due to formation of PbS
- ❖ Toxic in nature
- ❖ It is now replaced by Titanium oxide due to toxicity

2. Red lead Pigment (Sindur):

- ❖ Chemical Formula/name: Pb_3O_4 or $(\text{2PbO} \cdot \text{PbO}_2)$ - Triplumbic Tetraoxide
- ❖ Color: Red
- ❖ Used to prepare paints of different shades from orange red to brick red
- ❖ Insoluble in water
- ❖ Soluble in acids

3. Chrome Yellow Pigment:

- ❖ Chemical Formula: PbCrO_4
- ❖ Chemical Name: Lead Chromate
- ❖ Color: Yellow

- ❖ Occur in nature as Crocite
- ❖ Insoluble in water
- ❖ Soluble in nitric acid and caustic alkalis

4. Chrome Red Pigment:

- ❖ Chemical formula: $\text{PbCrO}_4 \cdot \text{PbO}$ or Pb_2CrO_4
- ❖ Chemical name: Basic Lead Chromate
- ❖ Color: Dark Red
- ❖ Used as red pigment

5. Turner's Yellow Pigment:

- ❖ Chemical formula: $\text{PbCl}_2 \cdot 4\text{PbO}$

6. Yellow Lead monoxide (Massicot):

- ❖ Chemical formula: Lead(II) oxide/ PbO

Plumbosolvency:

Plumbosolvency is the **ability of a solvent**, notably water, to **dissolve lead**. Due to toxic behavior of lead, this is an **undesirable property** for public supply of water. Plumbosolvency of water **can be countered** by achieving a pH of 7.5 by increasing the pH with lime or sodium hydroxide (lye), or by providing a **protective coating to the inside of lead pipes by the addition of phosphate at the water treatment works**.

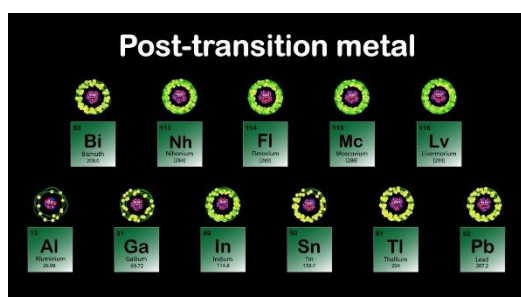
While optimal pH for prevention of plumbosolvency is 7.5, performance remains very good in the range pH 7.2-7.6. Achieving this pH has been shown to decrease population blood lead concentrations. Chlorinating water also reduces dissolved lead. It causes the interiors of lead pipes to become coated with lead chloride, which is very insoluble in cold water. However, lead chloride is fairly soluble in hot water. **For this reason, water that is to be used for drinking or the preparation of food should never be taken from a hot-water tap, if the water may have been in contact with lead. Water should be taken from a cold-water tap, and heated in a pan or kettle that does not contain lead or lead solder.**

Inert pair effect:

The inert pair effect is the tendency of the two electrons in the outermost atomic s-orbital to remain unshared in compounds of post-transition metals* (a set of metallic elements in the periodic table located between the transition metals to their left, and the metalloids to their right- list given below). The term inert pair effect is often used in relation to the increasing stability of oxidation states that are two less than the group valency for the heavier elements of groups 13, 14, 15 and 16. The term "inert pair" was first proposed by Nevil Sidgwick in 1927. The name suggests that the outermost 's' electrons are more tightly bound to the nucleus in these atoms, and therefore more difficult to ionize or share.

Lead is present down the 14th group, it also exhibits inert pair effect

*



(Post-Transition elements, exhibiting inert pair effect)