

REFERENCES TO SECTION 3

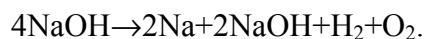
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4. PRODUCTION OF SODIUM, LEAD AND BISMUTH

4.1. SODIUM

Sodium is among the most abundant elements. Its content in the earth's crust is about 2.5 wt.%. The most important sodium compound, produced in the amount of millions of tons, is NaCl, the content of NaCl in seawater being about 3%.

Sodium can be produced by high-temperature reaction from almost any its compound (NaCl, NaOH, Na₂CO₃ and Na₂S). The method of sodium production that has enjoyed the widest application is electrolysis of the molten salts, for example:



Since water interacts with the one-half amount of sodium produced in this reaction, sodium yield cannot exceed 50% of theoretical value. In other electrolysis reactions, the yield of sodium could be even lower. Metallic sodium production by electrolysis of molten NaCl having melting point about 800°C is the most wide spread method. In order to reduce melting temperature such salts as CaCl₂, Na₂CO₃, etc. are used. For instance, mixture consisting of 40% NaCl and 60% CaCl₂ has melting temperature of 580°C, while mixture of 35.6% NaCl and 64.4% Na₂CO₃ melts at 600°C.

In electrolytic vat, the anode is usually made of graphite, the cathode being made of metal (Fe). Chlorine being by-product of this process is either discharged into atmosphere or accumulated for further using. Electric energy needed for sodium production is about 15 kW-h/kg Na.

Sodium produced by electrolysis contains 99.7 to 99.8% of basic metal and impurities (<0.1%K, <0.001% Fe, <0.15% Ca and others, such as Ba, Zr and Sn). It should be noted that the use of graphite electrodes causes sodium to be polluted with carbon. The worldwide sodium production data is given in Table 4.1 [4.1, 4.2].

TABLE 4.1. WORLD SODIUM PRODUCTION (thousand tonnes/year)

Years	1930	1952	1970	1990	2000 (prediction)
Quantity	25	140	270	354	340

4.2. LEAD

Lead content in the earth's crust is about $4 \cdot 10^{-3}\%$. The most important lead minerals are: PbS (86.6% Pb), $3\text{PbS} \cdot \text{Sb}_2\text{S}_3$ (58.8% Pb), PbCO_3 (77.55% Pb), $2\text{PbS} \cdot \text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ (42.4% Pb) and $\text{PbCl}_2 \cdot \text{PbCO}_3$ (76.0% Pb). Lead bearing ores such as PbS composition are the most abundant. In the oxidized (carbonate) ores lead exists in the form of PbCO_3 compound.

Only sulphide ores (PbSO_4 , PbS) are reprocessed in the lead-zinc industry using two ways, namely: hydrometallurgy and pyrometallurgy. Preference is given to the pyrometallurgical method, based on lead extraction by reducing or smelting. The molten lead contains copper, antimony, arsenic and sulphur impurities. Moreover, it usually contains silver extracted by lead purification. In order to remove impurities from the ore, the re-smelting is performed providing access for air (pyrometallurgical method). Impurities are oxidized with the products floating up to the surface and dumped away gradually [4.3–4.5]. The world lead production data is given in Table 4.2 [4.2, 4.6].

TABLE 4.2. WORLD LEAD PRODUCTION (M TONNES)

Year	1900	1950	1960	1970	1980	1990
Quantity	0.87	1.75	2.4	3.6	4.15	3.9

Commercial-grade (C1) lead contains about 99.985% of basic metal. Among the main impurities are Bi, Ag, Cu, Zr, As, Sn, Sb and Fe. Bismuth is withdrawn using Ca, Mg and Sb. Such impurities as Ca and Mg are injected into the vat filled with lead, resulting in production of Bi_2CaMg_2 compound, which is then removed, residual content of Bi in lead being equal to 0.008–0.01%. Upon adding Ca+Mg+Sb mixture and removal of slag, 0.003–0.04% Bi content is left in lead. Ca, Mg, Sb and Zn impurities are withdrawn by NaNO_3 oxidation in the presence of NaOH.

Being highly toxic lead may cause poisoning. Its maximum permissible concentration (MPC) values are 0.003 mg/m^3 and 0.03 mg/L respectively in air and water. The main contributors to the environmental pollution are releases from metallurgical plants, sewage (discharged to the world's ocean) and car engines. The value of annual lead release into the environment is presented in Table 4.3.

TABLE 4.3. AMOUNT OF ANNUAL LEAD RELEASE INTO ENVIRONMENT (THOUSANDS OF TONNES)

Source of release	Metallurgical plants	Car engines	Sewage
Amount	89	260	430–650

4.3. BISMUTH

Bismuth content in the earth's crust is about $2 \cdot 10^{-5}\%$. Bismuth deposits are few and far-between, bismuth recovering from the bismuth bearing ores being very complicated multistage process.

The major portion of bismuth is obtained by reprocessing polymetal copper ores and on the refining stage of lead production. Bismuth is extracted by adding Ca and Mg to molten lead. This results in formation of Bi_2CaMg_2 compound, which is considered as raw material for bismuth production.

Bismuth is applied in ferrous and non-ferrous metallurgy as admixture for stainless steel, pig iron and non-ferrous alloys. Alloys of Bi-Pb-Sn-Cd system are known for having 50–70°C and even lower melting temperature. The world bismuth production is given in Table 4.4 [4.2, 4.3, 4.8].

Market values of the aforementioned liquid metal coolants are summarized in Table 4.5.

The world-wide production of Bi is ~4000 t/a at a cost of ~\$ 12 per kg, its explored reserves as of 1972 being ~160 000 tons (coolant inventory of 1GW(e) reactor is 15.000 tons). Respective data for lead is: 4×10^6 t/a and $\sim 100 \times 10^6$ tons. Bismuth is expensive, its resources being limited. It is possible that its use could be confined to a limited number of reactors.

TABLE 4.4. WORLD BISMUTH PRODUCTION (tonnes/year)

Year	1959	1968	2000
Quantity	2355	3800 (except for Russia)	~ 5000 (forecast)

TABLE 4.5. MARKET VALUE OF LIQUID METAL COOLANTS (US\$/tonnes)

Coolants	1960	1998
Commercial-grade sodium	360	~ 700
Reactor-grade sodium ^{*)}	2500	4000
Commercial-grade lead	260	550
Reactor-grade lead	1000	3000
Bismuth	5000	12 000

^{*)} Stored in special tanks with argon cover gas.

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5. SODIUM AND LEAD TECHNOLOGIES

5.1. INTRODUCTION

The term "coolant technology" means a complex of methods and means assuring operation of facility under rated conditions and possible abnormal conditions. The main tasks related to coolant technology are as follows:

1. Development of coolant quality standards;
2. Analysis of impurities condition, their sources and accumulation rate in the circuit;
3. Analysis of corrosion and mass transfer;
4. Development of methods and equipment for keeping impurity content in the coolant within acceptable limits;
5. Analysis of different operating procedures and evaluation of related impurities input;
6. Control of coolant quality during operation.

Coolants produced by the industry (Na, Pb, etc.) do not always meet technological requirements. Therefore additional procedures are performed prior to filling circuit with the coolant in order to bring the coolant to required condition. Mounting and repair works are always required during facility life although resulting in pollution of the coolant. Another cause of changes in the coolant composition is corrosion, resulting in deterioration of mechanical properties of structural materials. Corrosion products are transported along the circuit, and depositions are formed that can affect hydrodynamics and heat transfer, and hence reliability of facility. All circumstances mentioned above lead to the necessity of permanent control over the impurities content and corrosion processes in the circuit.

The main elementary corrosion processes in the liquid metal are as follows:

1. Interaction of coolant with passive or oxide films-passivation or activation of materials.
2. Dissolving of steel components and their chemical interaction with non-metal impurities (oxygen, hydrogen, etc.).
3. Penetration of liquid metal into solid materials causing frontal and inter-granular corrosion.
4. Transport of structural material components along the circuit.

Interaction of Na, Pb and Fe with oxygen occurs by the following reaction:

