HIGHLY MINERALIZED BRINES AS A PROMISING RESOURSE OF BROMINE AND BROMINE PRODUCTS

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The technologies are selected and compared for the production of bromine and its compounds from the brines of the Znamensk deposit of the Irkutsk Region.

Brines, bromine extraction, lithium bromide, organic bromine compounds, gold

In the world practice, bromine is extracted from underground brines and saline water where its reserves are unlimited. By the data of Geological Survey (Mineral Commodity Summaries, January, 2002), the amounts of bromine produced in 2001 made up 513 th t, 204 and 200 th t of which were recovered in the USA and Israel, respectively. In Russia, production of bromine in the city of Perm fails to satisfy the demands of domestic industry; therefore, it is mainly imported from the countries of the Common Wealth of Independent States.

In 1998 the Ministry of Atomic Industry of Russia claimed hydrominerals of the Irkutsk Region (Russia) perspective for industrial production of lithium, bromine, magnesium, calcium, etc. which are necessary for enterprises of the atomic and other industries. The Irkutsk-Zhigalovsk gas-bearing region consisting of Znamensk, Kovyktinsk, and Omoloisk areas is among the first to exploit.

In the Siberian platform, highly mineralized brines, including the brine of Znamensk area, have the temperature over 30°C and the density of 1.23–1.32 t/m³, contain magnesium and calcium chlorides up to 95%. The pH value ranges from 4.5 to 5.9. Besides bromine and macrocomponents (Mg, Ca, Na, K), they comprise rare metals (Li, Rb, Cs, Sr) and microcomponents (I, B, etc.). The accompanying extraction of lithium would reduce the cost price of bromine, enlarge the range of marketable products, and put the brines in use for preparation of drilling fluids.

Despite this fact, brine deposits of the Siberian platform have not yet been developed due to their remoteness from industrial areas, considerable depth of occurrence, and severe climate. However, at the present time, the large oil deposits with accessory brines are developed in the Eastern Siberia. The “Russia Petroleum” Company performs geological prospecting in the Kovyktinsk deposit where aside from the natural gas field, the structural zones with hydromineral reserves are revealed.

The paper is aimed at substantiating the optimal technology of bromine extraction as applied to the brines of the Znamensk deposit (Irkutsk Region) representing a typical chloride calcium brine. The investigations were conducted by the “Iodobrom” Scientific-Production Union on demand of the “BrineSib” Innovation Firm (Irkutsk) in 1992–1994.

TECHNOLOGY OF BROMINE STEAM STRIPPING AFTER BROMIDE-ION OXIDATION

The steam stripping is used for industrial recovery of bromine from concentrated solutions of iron bromide and industrial product as well as from solutions obtained from carnallite, pharmaceutical and organic wastes [1].

To produce bromine from brines of the Znamensk deposit, the bromide-ion is oxidized by chlorine:

\[ \text{CaBr}_2 + \text{Cl}_2 \rightarrow \text{CaCl}_2 + \text{Br}_2, \]  

(1)

\[ \text{Br}_2 + \text{Cl}_2 \rightleftharpoons 2\text{BrCl}. \]  

(2)

In the stage of bromine steam stripping, conversion does not occur, and condensation of the air–steam mixture containing bromine, chlorine, and water steam is accompanied by separation of liquid bromine and water. As a result, marketable bromine of A or B type is produced.

To release free halogens from the brines, alkaline carbamide solution is used. In this case, the reactions proceed as follows:

\[ 3\text{Br}_2 + (\text{NH}_2)_2\text{CO} + 6\text{NaOH} = 6\text{NaBr} + \text{CO}_2 + \text{N}_2 + 5\text{H}_2\text{O}, \]  

(3)

\[ 3\text{Cl}_2 + (\text{NH}_2)_2\text{CO} + 6\text{NaOH} = 6\text{NaCl} + \text{CO}_2 + \text{N}_2 + 5\text{H}_2\text{O}. \]  

(4)

After rendering harmless, the excess of HCl is neutralized by limewater:

\[ 2\text{HCl} + \text{Ca(OH)}_2 = \text{CaCl}_2 + \text{H}_2\text{O}, \]  

(5)

\[ 2\text{HBr} + \text{Ca(OH)}_2 = \text{CaBr}_2 + \text{H}_2\text{O}. \]  

(6)

In the stage of bromine extraction, the blows-off are purified by alkaline carbamide solution (3) and (4) with bromine yield of 95%.

The disadvantage of the technology proposed is the necessity to employ liquefied chlorine, which is difficult due to complicated conditions of transportation, storage, and environmental safety. In order to improve the ecological and economical indices, it is expedient to oxidize bromide-ions by anode chlorine obtained directly in the deposit during electrolysis of brine [2, 3] or sodium chloride solution [4]. Diaphragm-free electrolysis is the most economical [3]. Owing to the saline deposits existing in the area where brines occur, chlorine is extracted from sodium chloride at small plants by diaphragm electrolysis (up to 10 th t/yr, 28 t/day). The process consists of three stages: dissolving and filtration of NaCl solution, electrolysis, cooling, and distillation of chlorine. The accompanying caustic alkali obtained can be used in complex treatment of brine.

Figure 1 presents the technological scheme of bromine extraction from brines by steam stripping.

**ION-EXCHANGE TECHNOLOGY OF BROMINE EXTRACTION**

Ion-exchange extraction of bromine is based on the capacity of anion-exchange resins to selectively sorb elementary bromine (oxidized form) from solutions. Penetrating into anionite phase, bromine as well as Cl\(^-\) and Br\(^-\) ions form complex ions of Br\(_2\)Cl\(^-\), Br\(_3\)\(^-\), and Br\(_5\)\(^-\) stronger adhered by anionite than Cl\(^-\) ions [1].

Bromine sorption requires highly alkaline anionites such as AB-17 (Russia), IRA-400 (Germany), Dowex 1×8 (USA), IMAC-54 and Kastel A 300 (Italy) [1] as well as weakly alkaline ones [1, 5]. Anionites in Cl\(^-\)- and Br\(^-\)-ion forms are the strongest absorbers.

Bromine is desorbed in treatment of anionite by sulfite and sodium chloride solution. Sulfite is the reducing agent for conversion of Br\(_2\) into bromide-ion, and chloride-ion is added for more complete change of Br\(_2\) to liquid phase [1]. In [5, 6], it is suggested to desorb bromine from anionite by steam or anionite boiling in water. In this case, thermostable resins are more preferable to use as sorbents, since they are hardly separable.