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Plant-Scale Method for the Preparation of Deuterium-Depleted Water

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A study of the utilization of aqueous decomposition of sodium amalgam for the production of deuterium-depleted water is presented. In the framework of this work the correlation between the deuterium content of the hydrogen gas and the concentration of the aqueous alkali, both formed in the reaction of sodium amalgam with water, is established. The sodium amalgam is prepared via sodium chloride electrolysis. In addition to the formation of an industrial alkaline solution containing 50% w/w sodium hydroxide, hydrogen gas with a deuterium concentration of 50 ppm is obtained. This hydrogen gas is suitable (e.g., via combustion) for the preparation of deuterium-depleted water used, e.g., in cancer therapy.

Introduction

The role of deuterium in the nuclear (power) industry is well-known, and numerous methods have been developed for the separation of deuterium-enriched compounds, especially for heavy water. Because, however, deuterium-depleted light water and its derivatives respectively have provided new perspectives in both cancer research and therapy,[1] the production of deuterium-poor water in large quantities has also gained importance.[2] Although deuterium enrichment and depletion are simultaneous processes, isotope separation techniques applied for obtaining deuterium-enriched products do not necessarily provide an economical method for producing deuterium-depleted water and its derivatives. At the same time, the separation of hydrogen isotopes would require the installation and maintenance of expensive technologies. The aim of our work was to provide an economical new technique for producing deuterium-depleted light water in large quantities. Therefore, current hydrogen gas producing technologies suitable for deuterium separation[3] have been studied for utilization. This paper presents a study of the utilization of aqueous decomposition of sodium amalgam formed in the course of sodium chloride electrolysis.

Methods and Materials

Under continuous operation and steady load, the technological parameters of sodium amalgam production were as follows: sodium chloride concentration, 300−310 g/L; decomposition potential, 4.4−4.6 V; current density, 6−9 kA/m^2; temperature, 60−90 °C; residual concentration of sodium chloride solution, 260−270 g/L; cathode, mercury; anode, Ti/RuO$_2$ chlorine-selective; amalgam concentration, 0.3−0.4% w/w sodium; temperature of amalgam decomposition, 90−100 °C; residual concentration of amalgam, 0.01% sodium.

Deuterium content determination of the of the gas obtained was performed by IR spectroscopy of the water formed followed by direct flame combustion of the hydrogen gas in an oxygen atmosphere and in air, respectively, or by catalytic conversion by means of a copper oxide catalyst. The oxidation techniques applied did not affect the conversion efficiency. Although in our previous experiments[3] two types of amalgam containing 0.3 and 3.0% w/w sodium have been used, in the present work, however, an amalgam obtained in an industrial NaOH-producing process was applied. This amalgam contained 0.3−0.4% w/w sodium. The reason for using this amalgam was that it could be handled as a liquid and thus could be easily withdrawn from the industrial apparatus (electrolytic cell). On the other hand, the isotope separation factor practically does not differ from the value obtained for the amalgam with 0.3% w/w sodium.[3]

Results and Discussion

The most important industrial technology for the production of sodium hydroxide is the aqueous decomposition of sodium amalgam formed during the electrolysis of sodium chloride. In the decomposition process a large amount of hydrogen gas is formed as well:

$$\mathrm{Na} + n\mathrm{H_2O} = \mathrm{Na^+} + \mathrm{OH^-} + {}^1\!/_2\mathrm{H_2} + (n-1)\mathrm{H_2O} \quad (1)$$

The results of our investigations indicate that the deuterium concentration of the hydrogen gas formed in the decomposition process is lower than that of the water used depending on the technological conditions. Thus, the production of various deuterium-depleted compounds is possible without application of further isotope separation techniques.

Of metal amalgams, lithium amalgam is applied for simultaneous separation of ^{6}Li−^{7}Li and H−D isotopes.[4]

Decomposition of sodium amalgam for the production of deuterium-poor hydrogen and water was investigated under conditions identical with the industrial parameters used for the production of aqueous alkali. At the same time, analysis of the samples obtained from the industrial technological process was also performed.

Isotope Separation Factors. The isotope separation factor is defined as the quotient of hydrogen/deuterium ratios in the gas and liquid phases:

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$$s = \frac{(\mathrm{H/D})_{\text{gas phase}}}{(\mathrm{H/D})_{\text{liquid phase}}} \tag{2}$$

The isotope separation factor (s) in the reaction of sodium amalgams with water is 3.47 at 90 °C. According to the results of our preliminary experiments,[3] at a constant Na content in the amalgam the value of the isotope separation factor does not depend on the deuterium content of the water and the amount of water decomposed. This observation is in agreement with the results obtained for other metals.[5,6]

On the basis of these results, it can be established that the hydrogen gas obtained in the aqueous reaction of sodium amalgam is suitable for the preparation of deuterium-depleted water.

Relations between the Deuterium Content and the Technological Parameters during Industrial Production. (a) Theoretical Considerations. Chemical parameters during the aqueous decomposition of the amalgam (such as temperature, pressure, and sodium concentration in the amalgam) can be considered to be stable within the ranges determined by the technological process. In the course of the decomposition, however, deuterium enrichment occurs in the liquid phase; thus, because of the constant separation factor, deuterium-depleted hydrogen gas with a continuous relative increase in its deuterium content is produced. The degree of water decomposition depends on the amount of amalgam and water. The same correlation holds for the concentration of the aqueous alkali formed. Because the concentrations of the alkali and deuterium contents of the hydrogen are inversely proportional to each other, for the selection of economically suitable reagent ratios a mathematical model should be deduced.

In the following section, the change in the deuterium content of the gas phase is studied as a function of the amount of amalgam and water.

After rearrangement of eq 2, the isotope separation factor of the decomposition process of the amalgams (reaction 1) is generalized for the gas and residual phases:

$$s = \frac{(n_g^H)(n_r^D)}{(n_r^H)(n_g^D)} \tag{3}$$

where n = number of moles, g, r = indices for the gas and residual phases, and H, D = indices for hydrogen and deuterium, respectively.

According to the mass balance of reaction 1, the amount of evolved hydrogen and deuterium produced by the metal amalgam reacted:

$$\frac{m_{Na}}{M_{Na}}E_{Na} = n_g^H + n_g^D \tag{4}$$

where m_{Na} = mass flow of sodium or the amount of sodium, M_{Na} = molecular (atomic) mass of sodium = 22.99, and E_{Na} = equivalent number of sodium in the aqueous reaction of sodium amalgam = 1.

Mass balance of deuterium and water as a function of mass flow or the amount of water used:

$$2\frac{m_w}{\bar{M}_w} = n_w^H + n_w^D \tag{5}$$

where m_w = mass flow of water or the amount of water, $\bar{M}_w$ = molecular mass of the water containing deuterium and hydrogen in a ratio corresponding to the initial conditions, and w = index for water.

The amount of hydrogen and deuterium in the residual phase of reaction 1 (in the form of water and dissolved hydroxides)

$$n_r^H = n_w^H - n_g^H \tag{6}$$

$$n_r^D = n_w^D - n_g^D \tag{7}$$

the mole number of deuterium in the hydrogen gas formed

$$n_g^D = m_g^D/M_D \tag{8}$$

and the mole number of deuterium in the original water

$$n_w^D = m_w^D/M_D \tag{9}$$

can be expressed by eqs 8 and 9.

Considering that the mass fraction value is the most general expression for characterizing the deuterium content, the amount of deuterium in the original water and in the hydrogen gas formed can be described by eqs 10 and 11:

$$c_g^D = \frac{m_g^D}{m_g^D + m_g^H} \tag{10}$$

$$c_w^D = \frac{m_w^D}{m_w^D + m_w^H} \tag{11}$$

Introducing the mole number values of hydrogen and deuterium in the gas and residual aqueous phases into eq 3 and then after reducing and rearranging eqs 4−11 and using the substitution described by eq 12:

$$\bar{M}_H/M_D = k_1 \tag{12}$$

we obtain eq 13.

$$s = \frac{\left(\dfrac{1 - k_1c_g^D}{k_1c_g^D}\right)}{\left(\dfrac{2\dfrac{m_w}{\bar{M}_w}(1 - k_1c_w^D) - \dfrac{m_{Na}}{M_{Na}}E_{Na}(1 - k_1c_g^D)}{2\dfrac{m_w}{\bar{M}_w}k_1c_w^D - \dfrac{m_{Na}}{M_{Na}}E_{Na}k_1c_g^D}\right)} \tag{13}$$

Equation 13 is the mathematical model of the deuterium distribution occurring in the aqueous decomposition of amalgams. In this expression the isotope separation factor is related to the mass flow of the feedwater and the amalgam, as well as to the deuterium content of the hydrogen gas formed. The deuterium concentration of the feedwater is considered to be known.

If eq 13 is applied for the description of the process characterized by eq 1, the deuterium concentration of the gas formed can be calculated. For calculation, parameters $\bar{M}_w$, s, E_{Na}, M_{Na}, and c_w^D for sodium are considered to be constant values, and the variables are the values of the mass flow of water and sodium, respectively. The relationship is a quadratic polynom.

Table 1. Influence of the Sodium Mass Flow Rate on the Deuterium Content of Hydrogen Gas and on the Concentration of Aqueous Alkali at a Feedwater Flow Rate of 1000 kg/h (Temperature = 90 °C; Na Content in Amalgam = 0.3% w/w; s = 3.47)

mass flow rate of sodium (kg/h)	deuterium content of gas (ppm)	concentration of alkali (% w/w)
50	45.0	8.3
150	46.3	22.8
250	47.7	35.1
350	49.2	45.6
450	50.7	54.7
550	52.4	62.7
650	54.2	69.6
750	56.1	76.4
850	58.1	81.5
950	60.4	86.6
1050	62.7	91.1
1150	65.3	95.2
1277	68.9	99.9

The concentration of aqueous alkali obtained in the decomposition process can also be calculated in this way.

(b) Experimental Results. Considering a feedwater flow rate of 1000 kg/h, in accordance with the stoichiometry the highest possible mass flow rate of sodium in amalgam is 1277 kg/h. At a feedwater flow rate of 1000 kg/h and at a sodium mass flow rate of 50−1277 kg/h, the expected deuterium concentrations of the stoichiometrical hydrogen gas formed are shown in Table 1 and Figure 1. Calculations were performed for gradually increasing flow rate values of sodium (division = 100 kg/h).

Data in Table 1 illustrate that in the range of sodium mass flow examined (50−1277 kg/h at a constant feedwater flow rate value of 1000 kg/h) the deuterium content of the hydrogen gas formed increased from 45.0 ppm to only 68.9 ppm. On the basis of these results, it can be established that the production of hydrogen with a deuterium concentration of 50 ppm can be realized simultaneously with the production of aqueous alkali containing 50% w/w sodium hydroxide. Thus, the industrial manufacturing procedures used for sodium hydroxide production are suitable, without technological modification, for the production of hydrogen gas with low deuterium content.

(c) Industrial Verification. During electrolysis in Borsodchem Corp. using 50% w/w sodium hydroxide, hydrogen gas with a deuterium concentration of 51−54 ppm has been obtained. This value corresponds to the concentration of 50 ppm obtained by the modeling process.

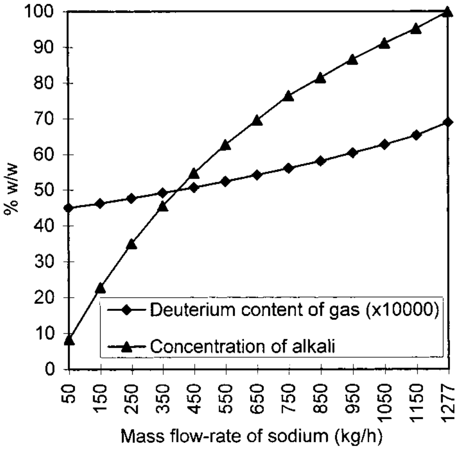

Figure 1. Influence of the sodium mass flow rate (feedwater flow rate, 1000 kg/h; temperature, 90 °C).

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