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TECHNICAL NOTE

HYDROGEN FROM BRINE ELECTROLYSIS: A NEW APPROACH

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Abstract—The electrolysis of brine yields chlorine, hydrogen and sodium hydroxide. In the conventional chlor-alkali industry, hydrogen is a by-product frequently burnt with chlorine to manufacture hydrochloric acid. It is suggested that the process can be made more advantageous if hydrogen is saved and chlorine is reacted with water (thermally or photocatalytically) in a second step to produce hydrochloric acid and oxygen. Large scale production of hydrogen by this method has several advantages. Vast quantities of sodium hydroxide may be necessary to control carbon dioxide emissions into the atmosphere from the burning of fossil fuels. Hydrochloric acid could replace sulphuric acid in the phosphate fertilizer industry.

Hydrogen obtained from the decomposition of water is an ideal means to store, transport and use solar energy [1–4]. Solar hydrogen production via photovoltaic/electrolytic systems [5–6] is most promising as a regenerative nonpolluting energy storage system. The standard technique considered most suitable for the production of hydrogen is alkaline electrolysis [2, 7] where oxygen and hydrogen are generated at two electrodes, i.e.

$$2\ H_2O + \rightarrow 2\ e^- \rightarrow H_2 + 2\ OH^-(\text{cathode})$$
$$H_2O \rightarrow 2\ H^+ + \tfrac{1}{2}\ O_2 + 2\ e^-(\text{anode}). \qquad (1)$$

An alternative electrolytic method for hydrogen production is the electrolysis of brine which yields chlorine instead of oxygen, i.e.

$$2\ H_2O + 2\ NaCl \rightarrow H_2 + Cl_2 + 2\ NaOH. \qquad (2)$$

The technology of the chlor-alkali industry is well established and the primary aim of this process is the manufacture of sodium hydroxide. Hydrogen generated as a by-product is usually burnt with chlorine to make hydrochloric acid (when chlorine is used for other purposes hydrogen is sometimes converted into ammonia by the Haber process). At present, the electrolysis of brine is not adopted for the large scale manufacture of hydrogen, because of the necessity of finding ways of disposing of or utilizing large quantities of sodium hydroxide and chlorine. In this note we point out that the chlor-alkali industry can be modified to yield hydrogen, sodium hydroxide, oxygen and hydrochloric acid by making chlorine to react with water in a second step, i.e.

$$2\ NaCl + 2\ H_2O \xrightarrow[\text{Electrolytic}]{} 2\ NaOH + Cl_2 + H_2$$
$$Cl_2 + H_2O \xrightarrow[\substack{\text{thermal or} \\ \text{photocatalytic}}]{} 2\ HCl + \tfrac{1}{2}\ O_2. \qquad (3)$$

Reaction (3) can be affected thermally or photocatalytically with aid of sunlight. The photocatalytic method is perhaps the most promising, it is well known that the irradiation of chlorine dissolved in water in the presence of TiO_2 liberates oxygen converting chlorine into HCl [8], via the following mechanism,

$$TiO_2 \xrightarrow{\text{light}} e^- + h^+$$
$$2\ H^+ + Cl_2 + \underset{\substack{\uparrow \\ \text{conduction band } TiO_2}}{2e^-} \rightarrow 2\ HCl \qquad (4)$$
$$2\ OH^- + \underset{\substack{\uparrow \\ \text{valence band } TiO_2}}{2\ h^+} \rightarrow H_2O + \tfrac{1}{2}\ O_2$$

where e^- and h^+ are the photogenerated electron and hole respectively.

The reserve of sodium chloride is practically inexhaustable and because of other depleting natural resources and environmental problems, hydrochloric acid and sodium hydroxide will find new applications. Hydrochloric acid could replace sulphuric acid in the phosphate fertilizer industry, the largest consumer of the worlds supply of sulphuric acid. Superphosphate manufacture depends on orthophosphoric acid made from apatite and sulphuric acid by the wet process [10]. Already methods are devised for the manufacture of phosphate fertilizers from apatite using hydrochloric acid [9–10]. As sulphuric acid is an expensive commodity, the alternative routes of beneficiation of apatite will have to be seriously considered in the near future, and hydrochloric acid offers the cheapest alternative.

An environmental problem that might require large quantities of sodium hydroxide is the control of the carbon dioxide emissions into the atmosphere from the

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burning of carbonaceous fuels. Measurements conducted over the past twenty-eight years show that the carbon dioxide level in the atmosphere is increasing at a rate 1.5–2.0 ppm per year [11–12]. If the carbon dioxide concentration is going to increase at this rate for the next 100 years, the Greenhouse effect is expected to cause an increase of the average global temperature by 4.5°C [11–12]. The consequences of this temperature increase are disastrous, the climate pattern will change with adverse effects for most parts of the world and the rise in the sea level could exceed 2 m. To remove the annual emissions of CO_2 via the reaction.

$$CO_2 + NaOH \rightarrow NaHCO_3, \qquad (5)$$

10^9–10^{10} tons of sodium hydroxide are necessary. Practically CO_2 removal can be effected by installing NaOH containing absorbers into the coal and oil burning plants (or it may be necessary to devise ways to keep the atmosphere 'washed' with NaOH). The large quantities of HCl produced can also be utilized to regenerate CO_2 from sodium bicarbonate and direct it to sealed greenhouses for growing crops at elevated rates (sodium chloride product in the reaction can be recycled). It is known that the yield from most crops more than doubles when greenhouses are enriched with CO_2 to a level 3–4 times the atmospheric concentration [13]. The burning of the biomass and trapping the evolved CO_2 in NaOH for feeding into the greenhouses will also control the CO_2 pollution and at the same time increase the agricultural production. Another advantage of the above two-step method for hydrochloric acid production is the saving of hydrogen for ammonia synthesis. Again any excess HCl could be converted into ammonium chloride which is also used as a fertilizer. Furthermore carbon dioxide extracted from $NaHCO_3$ and HCl when combined with ammonia yields urea.

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