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A NEW THERMOCHEMICAL SPLITTING CYCLE OF SODIUM CHLORIDE FOR CHLORINE AND SODIUM HYDROXIDE PRODUCTION

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Abstract

A new thermochemical closed cycle of sodium chloride for the preparation of chlorine and sodium hydroxide is presented in this paper. The optimum conditions of the main reactions in the cycle were obtained from a series of experimental results. The heat flow of the cycle system was calculated based on the related thermodynamic equations and data. The kinetic study of the heterogeneous reaction in the cycle was carried out by means of a thermogravimetric method. The result shows that the proposed cycle demonstrates an obviously energy-saving advantage over all the other methods of chlorine and sodium hydroxide productions. It may become economically competitive with the current electrolytic method in the future.

Keywords: chlorine, sodium hydroxide, thermochemical closed cycle

Introduction

Recently, Takeuchi [1, 2] proposed three kinds of thermochemical closed cycles for the preparation of chlorine and sodium hydroxide, which aroused much interest from the world of chemical industry. On the basis of our previous work [4, 5], a new thermochemical closed cycle using TiO_2 as the circulating medium is presented in this paper. The closed cycle consists of five reactions shown as follows.

$$NaCl+4/3HNO_3 \rightarrow NaNO_3+1/3NOCl+1/2Cl_2+2/3H_2O \quad (1)$$

$$1/3NOCl+2/3HNO_3 \rightarrow NO_2+1/6Cl_2+1/3H_2O \quad (2)$$

$$NaNO_3+1/2TiO_2 \rightarrow 1/2Na_2TiO_3+NO_2+1/4O_2 \quad (3)$$

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$$1/2NaTiO_3 + 1/2H_2O \rightarrow NaOH + 1/2TiO_2 \quad (4)$$

$$2NO_2 + H_2O + 1/2O_2 \rightarrow 2HNO_3 \quad (5)$$

The material flow in the thermochemical closed cycle is shown in Fig. 1.

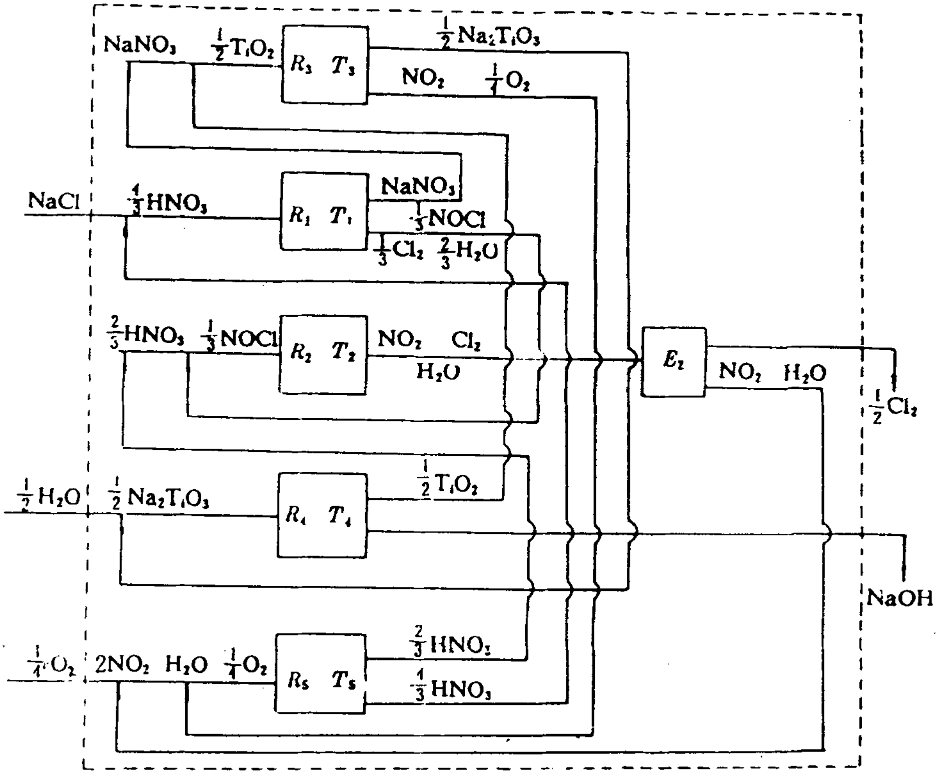

Fig. 1 TiO_2 system thermochemical splitting cycle of NaCl

Experimental

The most favourable conditions of the main reactions of the cycle were obtained through a series of experiments. The equilibrium yields of the products of the reactions are shown in Figs 2 to 5. The heat requirement (Q_{req}) for producing a definite quantity of Cl_2 with NaOH under the experimental conditions mentioned above was calculated by the thermodynamical free enthalpy function method [3].

Reaction (3) which takes an important part in the thermochemical closed cycle is a heterogeneous reaction. The condensed phase in the reaction has been

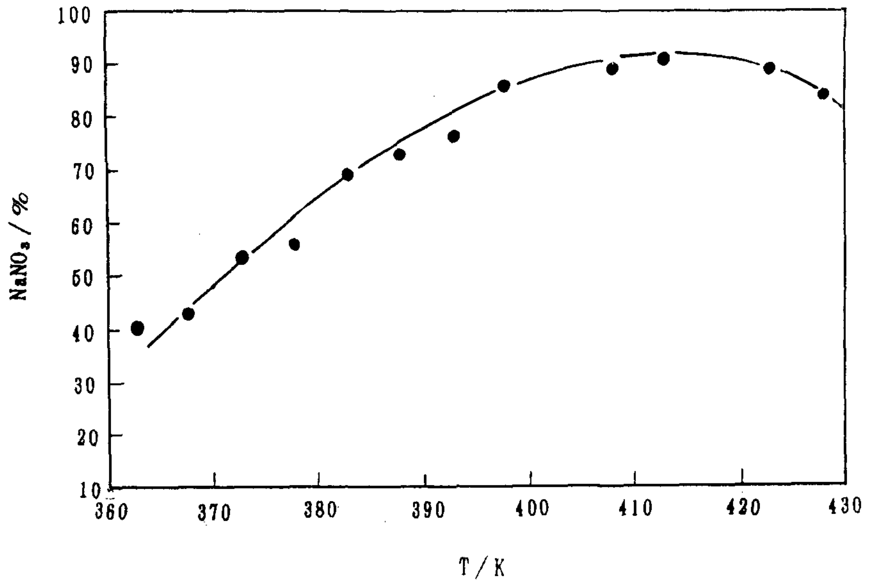

Fig. 2 Yield of $NaNO_3$ (%) *vs.* temperature (K)

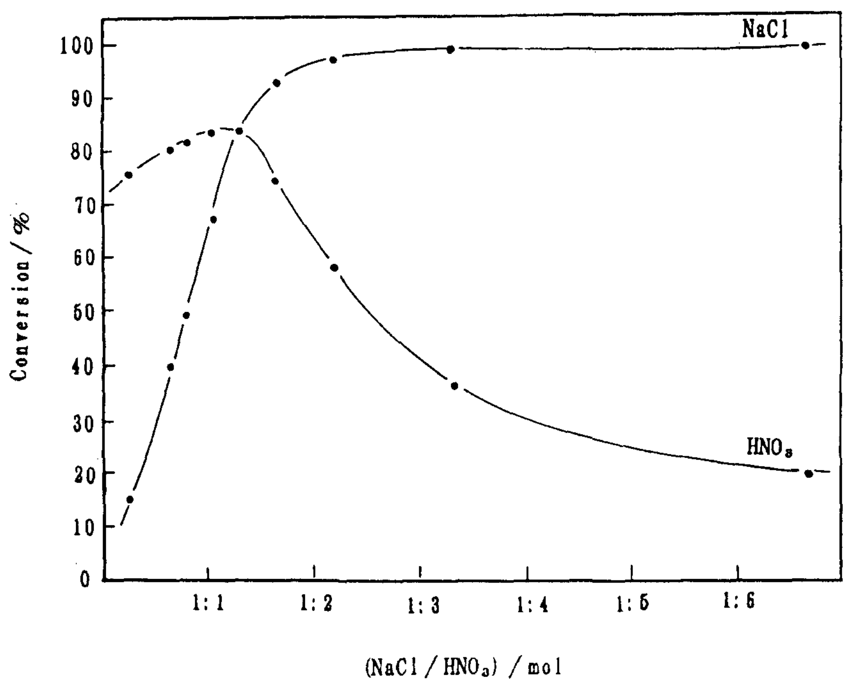

Fig. 3 Conversion of NaCl (or HNO_3) *vs.* $NaCl/HNO_3$(mol)

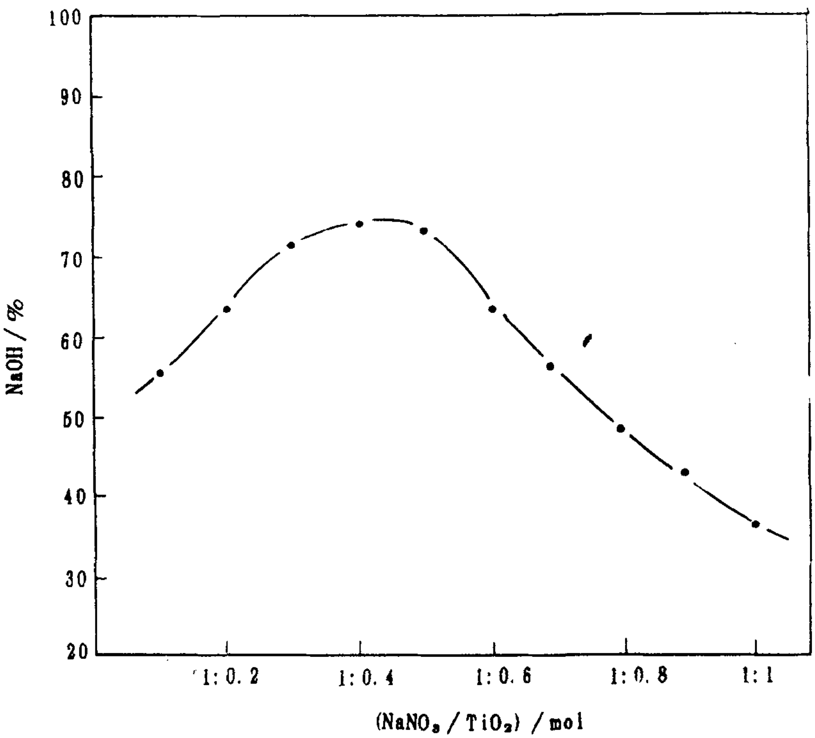

Fig. 4 Yield of NaOH (%) *vs.* $NaNO_3/TiO_2$(mol)

proved to be Na_2TiO_3 by the result of X-ray diffraction analysis, as shown in Fig. 6.

The data of TG and the data α (i.e.,$(W_o-W_t)/W_o$, where W_o is the initial weight of a reactant or product and W_t is its weight at time t) were obtained by thermogravimetry at several different temperatures ranging from 730 to 870°C. By plotting the function $g(\alpha)$ of eleven relevant kinetic equations *vs.* the time t respectively of which, two groups of curves obtained are shown in Figs 7 and 8.

Results and discussion

1. The proper temperature for reaction (1) in the closed cycle is 413 K and for reaction (3) is 1073 K.

2. Under the conditions mentioned above, the optimum initial mole ratios are found to be 1:3.333 for $NaCl/HNO_3$ and 1:0.5 for $NaNO_3/TiO_2$.

3. Under the conditions of 1 and 2, the conversion of NaCl is 99.7%, the yield of NaOH is 73.74%.

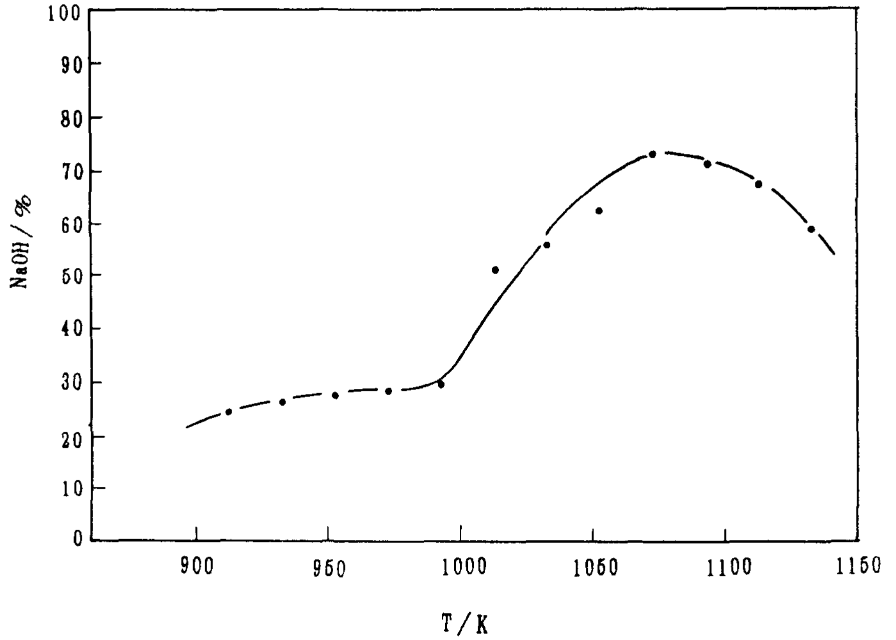

Fig. 5 Yield of NaOH (%) *vs.* temperature (K)

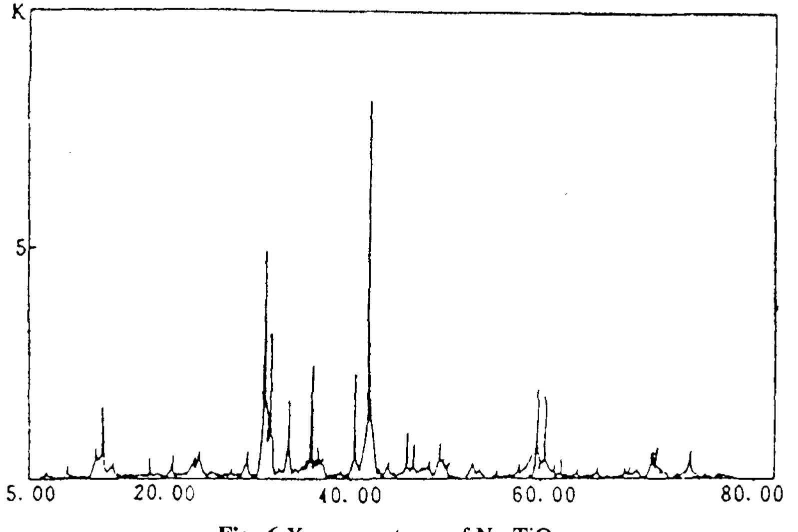

Fig. 6 X-ray spectrum of Na_2TiO_3

4. Figure 7 shows that the curves of function $g(\alpha)$ *vs.* t are all straight lines, obeying the following kinetic equation:

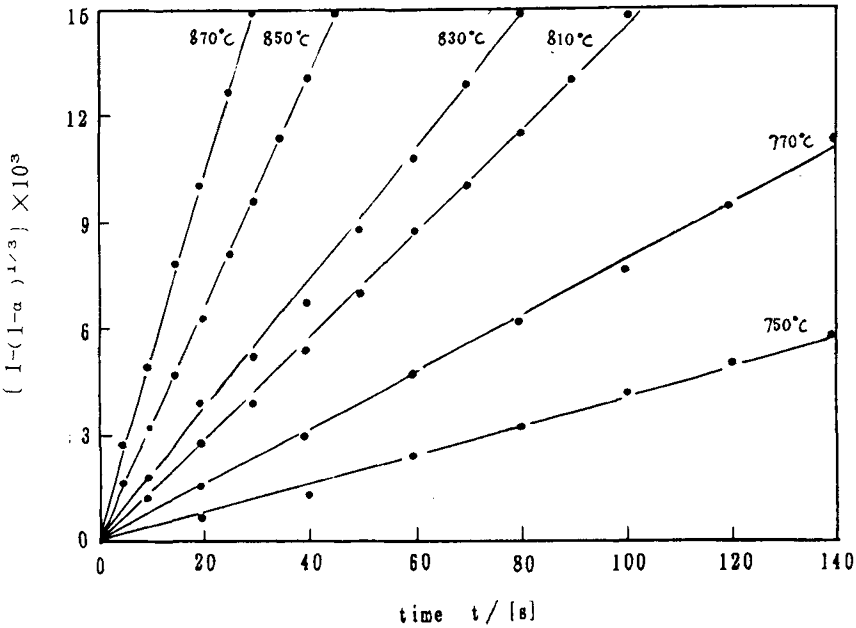

Fig. 7 Relation between $1-(1-\alpha)^{\frac{1}{3}}$ and t

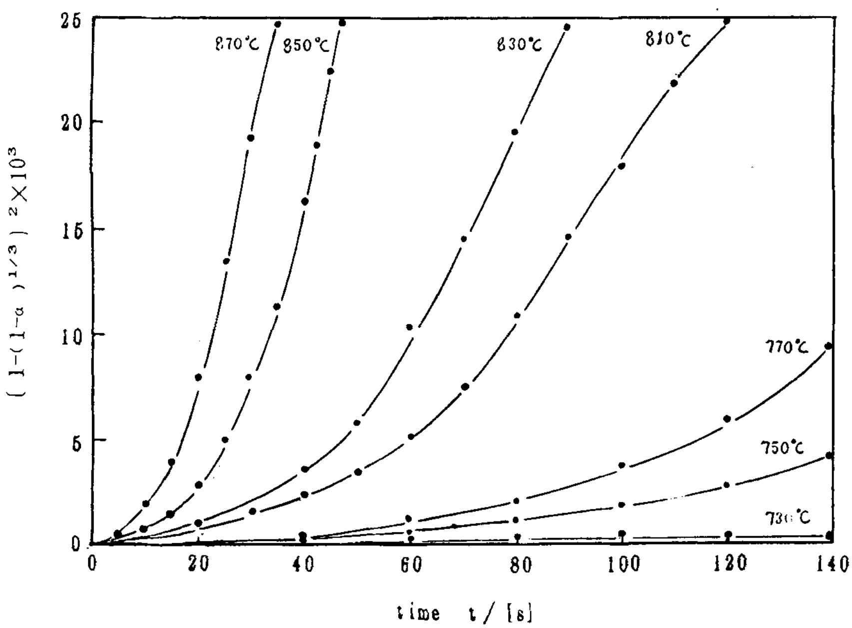

Fig. 8 Relation between $[1-(1-\alpha)^{\frac{1}{3}}]^2$ and t

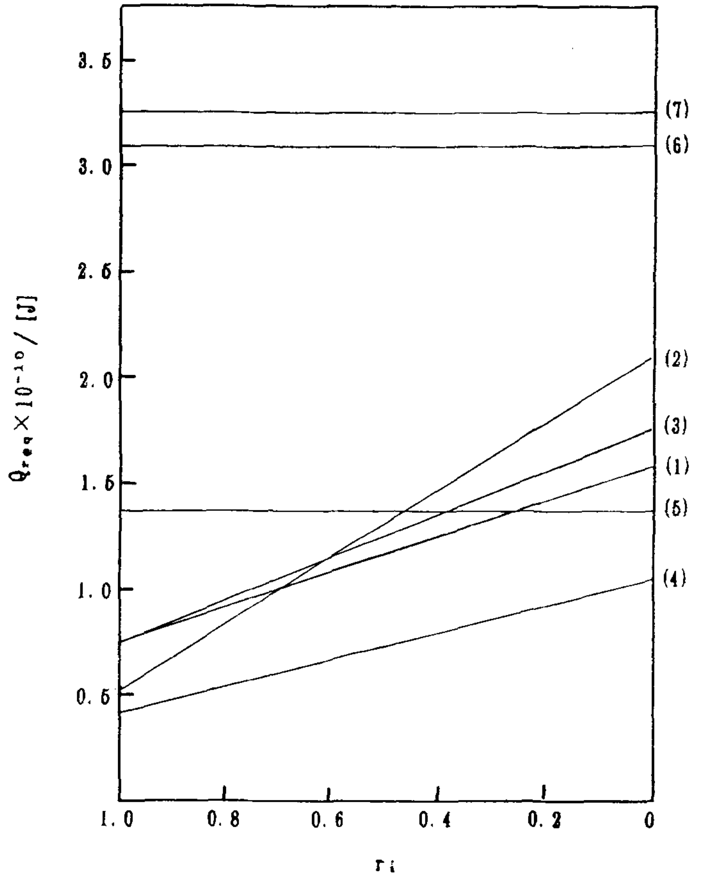

Fig. 9 Plot of Q_{req} *vs.* r_i; (1) Floride system cycle; (2) Borate system cycle; (3) Ferric oxide system cycle; (4) Titanium oxide system cycle; (5) Electrolytic method (theoretical value); (6) Ion exchange membrane method I; (7) Ion exchange membrane method II

$$1-(1-\alpha)^{\frac{1}{3}}=\frac{MkC_o^n}{\rho r_o}t \qquad (6)$$

That is to say, the interface chemical reaction is the controlling factor for reaction (3) over the entire temperature range of 730 to 870°C. However, Fig. 8 shows that the kinetic equation for diffusion is not obeyed for the reaction (3) for the same temperature range. This problem remains to be solved by further research.

5. According to the experimental conditions mentioned above, the heat requirement Q_{req} can be calculated by the relevant thermodynamic Eqs (7), (8) and (9) and the Funk equation (10).

$$\Phi'_T = -\frac{G^o_T - H^o_{298}}{T} = -\frac{H^o_T - H^o_{298}}{T} + S^o_{298} \tag{7}$$

$$\Delta\Phi' = \Sigma(\Phi'_T)_p - \Sigma(\Phi'_T)_r \tag{8}$$

$$\Delta G^o_T = \Delta H^o_{298} - T\Delta\Phi'_T \tag{9}$$

$$Q_{req} = \Sigma(\Delta H^o_T + Q_r) - \Sigma Q_p \cdot r_i \tag{10}$$

Figure 9 is the plot of heat requirement Q_{req} *vs.* heat regeneration ratio r_i, including the results obtained in this cycle and those of several other thermochemical cycles and methods found in literature [1, 2].

From Fig. 9, it could be seen that the heat requirement Q_{req} in this cycle is the least as compared with all those of other cycles and methods.

If the ratio of thermal regeneration r_i assumed to be 0.6, the heat requirement Q_{req} calculated in this work for producing 1000 kg of Cl_2 with 1126 kg of NaOH is 7.74×10^9 J, while in producing the same amount of Cl_2 and NaOH by electrolytic method, theoretical heat requirements calculated by Rossini is 1.372×10^{10} J, and the practical heat requirement is 3.012×10^{10}~3.054×10^{10} J.

In order words, for producing same amount of Cl_2 and NaOH, the heat requirement calculated by the authors on the basis of the result obtained in this work is only 56% of that of the current electrolytic method theoretically, but 25.3% of that of the latter method practically. By the way, the energy required for separation and transportation of the materials was not included in the calculation of this work.

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Zusammenfassung — Vorliegend wird ein neuer geschlossener Kreislauf von Natriumchlorid zur Herstellung von Chlor und Natriumhydroxid dargelegt. Anhand einer Reihe von Experimenten wurden die optimalen Bedingungen für die Hauptreaktionen dieses Kreislaufes bestimmt. Der Wärmefluß des Kreislaufsystemes wurde auf der Grundlage der diesbezüglichen thermodynamischen Gleichungen und Daten berechnet. Die kinetische Untersuchung der heterogenen Reaktion im Kreislauf wurde mit Hilfe der thermogravimetrischen Methode ausgeführt. Die Ergebnisse zeigen, daß der vorgeschlagene Kreislauf einen eindeutigen energiesparenden Vorteil gegenüber allen anderen Methoden zur Herstellung von Chlor und Natriumhydroxid bietet und wirtschaftlich gleichbedeutend mit der gegenwärtigen Elektrolysemethode werden kann.