

Experiments with Hydrogen-Exchange Zeolites for Preparing Acids¹

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Introduction

A recently developed artificial Zeolite, called Zeo-Karb,H² will exchange hydrogen ions for sodium or other base ions. The final zeolite, now containing sodium in place of hydrogen, can be regenerated by treatment with some acid such as hydrochloric or sulfuric. These reactions seemed to offer a possible new way of changing the sodium or other salts of acids, that are difficult to prepare, into the free acids. A good case where this process would be desirable, is perchloric acid from sodium or potassium perchlorate. Present methods³ of making perchloric acid are difficult. Briefly, the proposed process would consist in treating the hydrogen zeolite with sodium perchlorate, whereby a sodium zeolite and free perchloric acid would be formed. The sodium zeolite would be regenerated by treatment with hydrochloric acid.

The problem described in this paper was to determine the concentration and purity of the perchloric acid, the quantity of zeolite required, and the quantity of acid needed for regeneration.

Materials

The Zeo-Karb,H furnished by the Manufacturing Company,⁴ was a hard black granular substance. References in the literature indicated that it was made from coal by heating with acids. Apparently hydrochloric acid had been used as chloride was released to any percolating liquid.

The industrial use for this zeolite seems to be in purifying water whereby sodium as well as other base ions can be substituted in the water by hydrogen.

The carbonic acid, thus left in the water, can be removed by aeration. Then, the water will contain less total ions than when softened by any other method.

Experimental

In the preliminary experiments, hydrochloric acid was prepared from sodium chloride. In the first experiment, 10 grams of the Zeo-KarbH were placed in a buret which was then filled with normal sodium

¹ From a thesis as part of the requirements for an A.M. degree by Mr. Yancey.

² Chemical and Metallurgical Engineering, **46**:177 (1939). Industrial and Engineering Chemistry, **33**:1291 (1941).

³ Newnam and Mathers, Trans. Electrochemical Society, **75**:271 (1939).

⁴ Permutile Company, 330 W. 42nd Street, New York City.

chloride (58.5g/L). Every five minutes, solution, as shown in the table, was withdrawn from the bottom for analysis. The data are given in Table I.

TABLE I

Time in min.	Ml of acid collected	Normality of acid collected	Grams of HCl per ml. of sample	Percent of NaCl changed to normal HCl
5	4.6	.6228	0.0227	62.2
10	3.2	.3547	0.0130	35.7
15	12.0	.1634	0.0059	16.3
20	2.3	.1839	0.0067	18.4
25	1.6	.0715	0.0026	7.15
30	6.0	.0511	0.0129	5.11
35	1.8	.0715	0.0026	7.15

A survey of these data shows that the maximum concentration of acid produced was .6228, whereas normal acid should have been obtained, if exchange had been perfect. The normality decreased rapidly, thus showing small capacity of the zeolite. This maximum yield of acid was, therefore, only 62.2%, and the yield on the last sodium chloride passing through the zeolite was just 7.15%. The over all yield of hydrochloric acid for the total run using 31.5 ml. of N. NaCl on 10 g. of zeolite was 22.5%.

In the next series of experiments, 20 g. of zeolite were used, otherwise the experiments were made as before.

TABLE II

Time in min.	Ml of HCl collected	Normality of the HCl produced	Grams of HCl per ml. of HCl	Percent or the NaCl that was changed to HCl
5	3.0	.8781	.032	87.8
10	1.1	.6841	.0249	68.4
15	2.6	.5718	.02085	55.2
20	2.0	.4595	.01675	45.9
25	1.9	.3880	.01415	38.8
30	3.1	.3165	.01154	31.6
35	2.9	.2533	.00931	25.5
40	2.7	.2245	.00819	22.4
45	2.6	.2961	.0101	29.6
50	2.1	.0715	.0026	7.1
55	4.4	.1532	.0056	15.3
60	3.7	.1225	.0045	12.2
65	1.3	.1125	.0045	12.2
70	1.1	.1123	.0041	11.2

A survey of these data shows that maximum exchange to hydrochloric acid for the first contact, which, of course, should give the highest, was 87.8%. The total yield of hydrochloric acid from 34.5 ml. of N. NaCl on 20 grams of zeolite was 32%.

In Table III, 40 grams of zeolite were used, and the time of contact was reduced to 3 minutes.

TABLE III

Time in min.	Ml. of HCl collected	Normality of the HCl produced	Grams of HCl per ml. of HCl	Percent of the NaCl that was changed into N HCl
3	2.6	1.174	.04282	117.4
6	4.3	.8487	.0309	84.7
9	2.3	.6534	.02383	65.3
12	2.5	.5616	.02048	56.1
15	1.4	.5285	.01916	52.5
18	2.7	.4850	.01786	48.5
21	3.5	.4390	.01600	43.9
24	3.0	.4084	.01489	40.8
27	2.0	.3637	.0134	33.76
30	2.0	.3396	.0123	33.7

A survey of these data shows that the excess of zeolite gave up extra acid as shown by the normality of the first acid being 1.174.

The total yield of hydrochloric acid from the 26.3 ml. of N. NaCl was about 57%.

In the next experiments, normal sodium sulfate was used. The acid produced contained hydrochloric in every case, which showed that the zeolite had been activated with hydrochloric acid. Data were about the same as for hydrochloric acid.

A 0.25 normal solution of potassium perchlorate at 30° was tried. The small solubility of this salt required this temperature and concentration. Twenty ml. of this solution were stirred with 10 grams of zeolite for 15 minutes and filtered. The per cent conversion was 77.6. This was not analyzed for hydrochloric acid, which, undoubtedly, was present. The same experiment, except at 55°, showed a 167.6 percent yield of acid. This of course meant a large liberation of hydrochloric acid from the zeolite. There was no difficulty in regenerating the zeolite.

All the above experiments showed that the method proposed would not be satisfactory for the preparation of any acid.

(1) In no case did a conversion approach completion.

(2) The solutions produced were impure due to release of some of the acid ions used in activating the zeolite.

(3) The solutions produced were more dilute than is desirable for ordinary use.