G.P.-S.21350—1937—2,000.

F.R. 5.

U1/D/3/2

BRANDSTOF-NAVORSINGS-INSTITUUT

VAN SUID-AFRIKA.

FUEL RESEARCH INSTITUTE

OF SOUTH AFRICA.

ONDERWERP :
SUBJECT : ____A CONTRIBUTION TO THE STUDY OF THE PRODUCTION

____OF CARBONACEOUS ZEOLITES FROM BITUMINOUS COAL.

AFDELING :
DIVISION : ____CHEMISTRY

NAAM VAN AMPTENAAR :
NAME OF OFFICER : ____C. C. la GRANGE

FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

REPORT NO. 12 OF 1944.

A CONTRIBUTION TO THE STUDY OF THE PRODUCTION OF

ZEOLITES FROM BITUMINOUS COAL.

SUMMARY.

(1) This report describes work done at the Institute to ascer-
tain whether South African coals could be used in the preparation
of carbonaceous zeolites.

(2) The products have been prepared by subjecting coal samples
to the action of gaseous sulphur trioxide in a rotary retort.

(3) It has been found that highly active products could be
obtained from all the coals tested, and activity alone could not
be used as a basis of discrimination.

(4) Theoretically a zeolite could operate for an indefinite
number of cycles, and in practice the chief factor preventing its
indefinite use is the unavoidable loss of zeolite, mainly through
attrition.

(5) The resistance of zeolites to attrition is therefore very
important. Tests seem to indicate that this can be increased by
activation to a practical degree only and by choosing hard coals
as raw materials.

(6) Since it is considered that sodium-zeolites possess advan-
tages in small plant where laboratory control and skilled operators
are not available, the conversion of hydrogen-zeolites to sodium-
zeolites has been studied in greater detail and a satisfactory
conversion process has been developed.

(7) It has not been found possible to conduct larger scale tests
on zeolites prepared from South-African coals.

INTRODUCTION.

The application of bituminous coal as a raw material for the production of zeolites is of comparatively recent date. No reference to such an application has been found in literature previous to 1935. The available information is largely confined to patent literature and only a few, more or less detailed papers have appeared. According to these papers and patents bituminous coal can be treated with sulphuric acid, oleum, chlorsulphonic acid, SO3 and other oxidising agents such as FeCl3 and Cl2 to produce a material having base-exchange properties. The available papers, however, deal only with the treatment of the coal with sulphuric acid, SO3 and similar sulphur containing agents. The production and the application of carbonaceous zeolites is covered by South African patents 412/35, 601/38, 96/42, 169/42 and 356/42.

The zeolite as produced operates on the hydrogen-cycle, i.e. exchange takes place between metal ions in solution and active hydrogen ions of the zeolite. In this cycle the zeolite is generally reactivated by treating it with dilute mineral acid. It is stated that the zeolite can be converted to operate on the sodium cycle by regenerating the spent zeolite with sodium chloride solution.

The object of the present investigation was to determine whether South African coal would provide a suitable raw material for the production of zeolites.

ANALYTICAL METHODS.

In the absence of a standard specification for testing zeolites the available literature was consulted and methods described by Beaton and Furnas [1], Broderick and Bogard [2], Broderick and Hertzog [3] and the American Waterworks Association [4], were followed as closely as possible. These tests comprise inter alia a determination of activity or capacity and a determination of the abradability of the zeolite.

A procedure described by Beaton and Furnas [1] and based on the removal of copper from a copper sulphate solution in contact

with a zeolite, was adopted with some modification to serve as a preliminary test of the activity or capacity of sulphonation products. Certain samples were selected for a more detailed and accurate determination of capacity. In this determination the procedure described by Broderick and Bogard and the American Water-works Association was followed as closely as possible. The zeolite is placed in a vertical tube and water of standard hardness is passed through the zeolite bed. The spent zeolite is regenerated with dilute acid (hydrogen cycle) or sodium chloride solution (sodium cycle) and the test is repeated until a constant working capacity value is obtained.

The capacity (grains/cub.ft.)

$$= \frac{\text{(Volume of soft water produced (galls) x Hardness of original Water (grains/gall)}}{\text{(Volume of Zeolite sample used (cu.ft.)}}$$

A rapid method for determining the attrition or hardness index of zeolites has been proposed by Broderick and Hertzog [3] and has been included in the Tentative Manual of Zeolite Test Procedures of the American Waterworks Association [4]. This method was followed with minor alterations in the present investigation. A more or less arbitrary index value having comparative value is obtained. Broderick and Hertzog state that the following meaning may be attached to attrition index values:

	Order of Attrition Index
Very soft substance	1100
Medium	340
Hard	49

A detailed description of the methods need not be given since the published methods were followed sufficiently closely. A few commercial zeolites were also subjected to the same test procedure so as to obtain comparable results.

COAL SAMPLES AND THEIR PREPARATION.

The size of commercial zeolite varies between 14 and 52 mesh (B.S.S.) and the samples treated would have to be crushed to a

similar/.......

similar size. It was therefore considered advisable to determine whether duff coal would represent a suitable raw material.

Eight samples of duff coal were procured and a screening analysis and proximate analysis of these samples are given in Table I.

TABLE I.

SCREEN ANALYSIS AND PROXIMATE ANALYSIS OF DUFF COAL SAMPLES.

Sample Number	Screen analysis (B.S.S.sieves)			Proximate Analysis		
	+ 14 mesh	-14 + 52	-52 mesh	Ash %	Moisture %	Vol.Mat.%
B	48.2	36.6	15.2	23.4	2.2	23.2
C	67.4	25.3	7.3	16.0	2.8	24.9
D	83.9	9.9	6.2	14.3	2.5	25.2
G	13.8	51.1	35.1	12.1	0.8	18.6
J	71.5	20.3	8.2	17.7	6.7	26.3
K	65.4	23.8	10.8	18.0	1.9	26.9
L	77.8	15.9	6.3	12.3	1.7	10.0
M	77.0	15.7	7.3	14.9	2.6	29.7

Four other samples of coal were also procured, crushed and the size fraction -25 + 36 mesh B. S.S. used in sulphonation tests. Analytical data on these samples are given in Table 2.

TABLE 2.

PROXIMATE ANALYSIS OF 4 COAL SAMPLES.

Sample Number	Type of coal used	Proximate Analysis		
		Ash %	Moisture %	Vol.Mat.%
A	Washed peas	13.7	2.6	27.9
E	Nuts	21.1	5.8	26.9
F	Washed nuts	11.0	1.1	31.1
H	Cobbles	12.0	1.9	25.0

These 12 samples were regarded as reasonably representative of the types of coal mined in South Africa. In order to be able to determine the effect, if any, of the ash constituents of the coal on the quality of the product, portions of three of the

above/......

above samples, viz. B, E and K were cleaned by washing at S.G. 1.6.
An analysis of the floats at S.G. 1.6 will be found in Table 3.

TABLE 3.

PROXIMATE ANALYSIS OF FLOATS AT S.G. 1.6

Sample Number	Float at S.G. 1.6 - %	Proximate	Analysis	
		Ash %	Moisture %	Vol.Mat. %
B[1]	82.8	9.4	2.6	27.4
E[1]	67.3	9.4	7.3	28.9
K[1]	83.5	10.1	2.7	28.4

In all tests -25 + 36 mesh material was used for sulphonation.
Products were numbered, using the letter of the coal sample and a
figure to indicate the number of the test. Thus A_3 means the
product obtained in the third test on Sample A.

PRELIMINARY TESTS.

Sulphuric Acid Reagents:

In preliminary tests the coal was treated with concentrated
sulphuric acid, oleum, chlorosulphonic acid and sulphuric acid
with added potassium dichromate. Although the weight ratio of
coal to acid was increased to 1: 10 the mass tended to froth and
cake to a considerable extent. The products obtained had poor
activity as determined by the copper sulphate method. This type of
reagent was therefore abandoned.

Sulphur Trioxide:

Preliminary tests with sulphur trioxide were done in a
closed vessel provided with a stirrer to which solid SO_3 was
admitted at intervals. The results with this apparatus were
also disappointing.

Better results were obtained when SO_3 was admitted to this
apparatus, and gaseous reaction products were withdrawn from it
continuously. The results were, however, erratic and this
appeared to be due to the abrasion caused by the stirrer. A
considerable proportion of - 36 mesh material was formed and this
tended to be more active by the $CuSO_4$ test than the + 36 mesh
material.

A /........

A rotary retort was then made which gave satisfactory results so that all subsequent experiments were done in this apparatus.

Sulphonation Apparatus.

The design of this apparatus which is shown diagrammatically in Figure I. was largely based on that used by Broderick and Bogard [2]. Sufficient data are given in the figure so that the apparatus need not be discussed in detail.

The platinized asbestos was prepared by soaking gooch asbestos, from which the finest fibres had been removed by washing, in platinic chloride solution, drying and igniting in the reaction tube at $500^{\circ}C$. Finally the reduction was completed by passing air, saturated with methyl alcohol vapour through the tube.

Sulphur dioxide and oxygen were taken from storage bottles and passed over the catalyst in the volume ratio of 2 : 1 respectively. The catalyst was heated electrically to the reaction temperature but as soon as the reaction set in, it proceeded with such vigour that no further external heating was required. The speed at which SO_2 was admitted could not be increased beyond 3000 c.c. per minute in order to keep the reaction temperature below $500^{\circ}C$.

The initial activity of the catalyst was not determined, but it did not seem to decrease appreciably and when measured towards the end of the investigation the conversion of SO_2 to SO_3 was 89% at a rate of 1000 c.c. of SO_2 per minute.

Reaction Conditions.

In all the tests 200 grams of air dry coal (-25+ 36 mesh) were charged to the retort.

The retort was rotated at 11 r.p.m.

The reaction temperature was generally $160^{\circ}C$. This figure was chosen after consulting the work of Broderick and Bogard [2] and doing a few preliminary tests. The rate of the SO_3 was adjusted so that no, or only a small quantity of SO_3 should escape unused, and was, of course, limited to a maximum of 3000 c.c./minute by the capacity of the platinized asbestos.

It/.......

It was also not feasible to check it entirely so as to maintain the Pt-catalyst at a reasonable reaction temperature.

In practically all experiments the pressure in the reaction vessel was atmospheric (about 650 m.m. Hg.) as the apparatus was not designed for any higher pressure. The sulphonation time was generally 310 minutes. Some of the results of preliminary tests are shown in Table 4.

TABLE 4.

RESULTS OF PRELIMINARY TESTS IN ROTARY RETORT.

Product Number	Sulphona-tion Time (mins.)	Temp. in Retort °C	Yield (% on dry coal)			Activity of + 36 mesh material (CuSO4 method) (grm Cu/grm dry Zeolite)
			+ 36 mesh	- 36 mesh	Total	
A 19 *	280	160	115.7	7.7	123.4	0.0576
A 26	310	160	117.1	4.6	121.7	0.0574
A 22	340	160	118.7	5.1	123.8	0.0572
A 25	400	160	116.1	7.7	123.8	0.0610
A 23	310	190	113.6	4.6	118.2	0.0550
A 24	310	130	122.5	6.2	128.7	0.0532
A 27 •)	310	160	114.5	7.7	122.2	0.0520

* Test conducted at 750 m.m. Hg. pressure as against 650 in other tests

•) A mixture of dry SO3 and HCl gas was used in this test.

The choice of the above reaction conditions was largely based on the results of these preliminary tests. No claim is made that the conditions chosen were optimum conditions for any coal.

Working up Reaction Products and Results.

In all the tests SO3 was used up rapidly at first. At a given time, varying from coal to coal SO3 absorption decreased appreciably and SO3 began to appear in quantity in the exit gas. The SO3 current was then decreased to a minimum of 500 c.c./min., while the test was allowed to proceed, usually to a total time of 310 minutes. The point where the SO2 first reached 500 c.c./min. was designated by "apparent saturation point". Moisture was given off from the charge during the whole experiment and the product was finally found

to be/....

to be "wet" containing an appreciable quantity of sulphuric acid. In order to remove the acid the product was washed three or four times by decantation. It was then transferred to a Buchner funnel where it was washed by adding distilled water about 10 times, and sucking dry after every addition of water. Even this thorough washing failed to remove the last traces of sulphuric acid.

During the washing a quantity of product was inevitably lost as very fine material running through the filter. The product was finally dried at 105°C and then screened to determine its content of - 36 mesh material.

The SO2 consumption was determined from the flowmeter which was checked by weighing the SO2 container before and after a test.

The following example may serve to show how the tests were conducted and the SO2 consumption was calculated.

Test L 4:

Weight of air dry coal used (grms)	=	200
Moisture content (%)	=	1.7
∴ Weight of dry charge (grms)	=	196.3
Average Room temperature (°C)	=	18
Atmospheric pressure (m.m.Hg.)	=	653
Reaction Temperature (°C)	=	160
Pressure in Retort	=	atmospheric
Flowmeter correction factor	=	0.8
Density of SO2 at N.T.P. (grm./l)	=	2.927

Test Period (p) mins.	SO2 under pressure (at flowmeter) of: (a) mm.Hg	Flow-meter reading (b) l/min.	Volume of SO2 at N.T.P.		Wt. of SO2. (grms.)	Wt.SO2 on dry coal (%)
			Uncorrected $(p \times b \times \frac{653+a}{760} \times \frac{273}{273+18})$ (litres)	Corrected (Uncor. x 0.8) (litres)		
0- 5	5	24	1.3	5.4			
5-10	5	28	2.0	8.4			
10-35	25	32	2.5	52.8			
35-85	50	36	3.0	127.5			
85-95	10	32	2.5	21.1			
95-105	10	30	2.0	16.9			
105-115	10	27	1.5	12.6			
115-125	10	26	1.0	8.4	-- Apparent Saturation		
125-310	185	30	0.5	78.0	62.4	182.6	93
Total			331.1	264.9	775	394
Used in period up to apparent saturation						301

Sulphonation under Standardised Conditions.

The results of tests on the coal samples are tabulated in

Table 5:

TABLE 5.

SULPHONATION TESTS ON COAL SAMPLES.

Test	Duration of Sulphonation (min.)			Calculated on dry coal charged						Activity + 36 mesh material (CuSO4 method) (g.Cu/g dry zeolite)
				SO2 Consumption (% Weight)			Product yield (% Weight)			
	Apparant Saturation	After.	Total.	To app. Satura. tion	After.	Total.	+ 36 mesh.	- 36 mesh.	Total.	
A26	140	70	310	357	87	444	117	5	122	0.0574
B 1	125	185	310	291	93	384	97	17	114	0.0592
B¹2	155	155	310	377	78	455	112	11	123	0.0590
C 1	205	105	310	364	54	418	89	19	108	0.0586
D 1	170	140	310	364	70	434	100	16	116	0.0598
E 1	200	110	310	296	57	353	101	11	112	0.0548
E¹2	145	165	310	318	88	406	109	9	118	0.0564
F 1	210	100	310	585	50	635	119	8	127	0.0592
G 1	185	125	310	371	62	433	93	36	129	0.0594
H 1	160	150	310	393	75	468	117	7	124	0.0618
H 2	155	155	310	397	78	475	118	5	123	0.0602
J 2	115	195	310	260	104	364	100	8	108	0.0578
K 1	130	180	310	285	91	349	110	7	117	0.0586
K¹2	170	140	310	376	71	447	118	7	125	0.0606
L 1	110	200	310	224	99	323	119	13	132	0.0616
L 4	125	185	310	301	93	394	122	11	133	0.0620
M 1	170	60	230	408	30	438	113	5	118	0.0522

With the exception of sample M 1, which was purposely prepared
to have a medium activity only, the activity of all the products is
reasonably uniform and quite high if 0.059 is considered an average value
for commercial zeolites (Beaton and Furnas [1]). Because of their
uniformity these activity values could not be chosen as a basis of
selection of products for further work.

The reproducibility of results is shown by tests H 1 and H 2.

Washing the coal before sulphonation does not seem to have a
very marked effect on the activity of the products. This is evident
from a comparison of samples B1 and B¹2, E1 and E¹2, K 1 and K¹2.

It was not possible to subject all these products to more
detailed tests and consequently samples C 1, H 1, J 2 and L 4 from

four typical coals were selected (more or less on the basis of SO_2 consumption during sulphonation) for this purpose.   A larger bulk sample of sulphonated coals was made up by combining samples A19, A22, H 2, $K^1 2$ and L1.   This bulk sample was numbered CZ for future reference.

Full capacity tests on the hydrogen- and sodium-cycle, as well as attrition index determinations were done on these samples and the results are shown in Tables 6 and 7, where values for commercial products are also given for comparison.   The commercial carbonaceous zeolite is indicated by the symbol "Karb" and the commercial mineral sodium zeolite by NaZ while a sample of B.D.H. Permutit is designated by B.D.H.P.

The products all had higher capacities than the commercial products.   On the other hand they showed considerably greater swelling on wetting and rather inferior hardness characteristics. It appeared possible therefore that they had been over-activated.

The treated water in the sodium cycle had an appreciable hardness, so much so that the end point of the capacity test had to be arbitrarily chosen as that point where an appreciable increase in hardness of the treated water was just evident, instead of determining the end point at a definite hardness e.g. 10 as stipulated in the testing methods consulted.

Generally the average hardness of the treated water was highest for zeolites showing the highest activity.   It will be shown later that the hardness of the treated water largely depends upon the degree of regeneration of the zeolite.

A more serious matter in connection with these carbonaceous sodium zeolites was that the treated water always contained some free acid towards the end of a cycle (up to 70 p.p.m. as $CaCO_3$). Sodium exchanger plant is not usually built to handle water containing free mineral acid and the presence of such acid would cause corrosion trouble.   The acid would have to be neutralised in any case before the water left the plant.   As sodium exchangers would probably find wider use in small installations than hydrogen exchangers. A more detailed study of the production and working of the former was made.

TABLE 6.

CAPACITY OF ZEOLITES IN HYDROGEN-CYCLE AND ATTRITION INDEX.

Sample Number	Bulk Density (gram/cc.)	Activity (grm Cu/ grm.dry Zeolite)	Swelling on Wetting. (Vol.%)	Capacity of Zeolite (grains CaCO3/cu.ft) Air Dry	Wet Swollen	Average Hardness of treated water (ppm. Ca CO3)	Chemical Efficiency [x] 1b.HC1 per kilograin CaCO3 removed.	(Equiv. Cations removed) ÷ (Equiv. HCl for regeneration) X (%)	Duration of Sulphonation after apparent saturation point. (mins.)	Attrition Index
Karb.	0.991	0.045	11.1	11,200	10,000	3	0.183	56.8	-	774
CZ	0.699	0.0595	27.4	16,600	13,000	4	0.124	84.2	155	2977
G1	0.745	0.0594	31.9	16,800	12,700	4	0.122	85.2	125	1348
H1	0.666	0.0618	46.5	16,800	11,500	4	0.122	85.2	150	1670
J2	0.740	0.0578	46.2	16,000	10,900	1	0.128	81.2	195	4049
L4	0.683	0.0620	31.2	16,400	12,500	3	0.125	83.2	185	2939

x The chemical (or salt, or acid) efficiency of a zeolite is defined as the ratio between the weight of sodium chloride (or the weight of acid) that is equivalent to the capacity generated in the zeolite, to the actual weight of salt(or acid) used for regeneration. Thus e.g. the theoretical equivalent of 1000 grains hardness (as CaCO3) is 0.167 lbs pure sodium chloride.
Therefore:

$$\text{Salt efficiency \%} = \frac{0.167}{\text{lbs. of salt used per 1000 grains capacity of regenerated zeolite}} \times 100$$

TABLE 7.

CAPACITY OF ZEOLITES IN SODIUM-CYCLE.

Sample Number	Bulk Density (grms/cc)	Swelling on Wetting (Vol.%)	Capacity (grains CaCO3/ cub.ft. zeolite)		Avg. Hardness of treated water (p.p.m. CaCO3)	Chemical lb. NaCl/Kilo grain CaCO3 removed	Efficiency (Equiv. Ca and Mg. removed) ÷ (Equiv. NaCl for regeneration) %
			Air dry zeolite	Wet-swollen zeolite			
CZ	‒	27.4	10,300	8,100	9	0.243	68.8
G 1	‒	31.9	11,600	8,800	13	0.216	77.4
H 1	‒	46.5	12,700	8,700	12	0.197	84.8
L 4	‒	31.2	11,500	8,800	12	0.217	76.8
NaZ	1.159	0	6,900	6,900	0	0.362	46.1
B.D.H.P.	1.393	0	4,100	4,100	0	0.610	27.4

FACTORS AFFECTING THE CAPACITY AND ATTRITION VALUES.

(a) Pre-oxidation:

It was evident from experimental work that the SO_3 used for sulphonation largely acts as an oxidising agent. Accordingly, some tests were conducted in which the coal was oxidised with air prior to subjecting it to sulphonation. The products obtained in these tests had poor activity, as well as high attrition values and the matter has not been followed up further.

(b) Duration of Sulphonation.

The duration of sulphonation affects both the capacity and the attrition index as shown by the results given in Table 8. The attrition index of products from coal L was already too high at a stage where the capacity was still comparatively low.

(c) Effect of Trommeling:

Tests were conducted to determine whether better results could be obtained by subjecting either the coal before sulphonation or the sulphonated product to controlled attrition by trommeling for fixed periods. Such a process would tend to produce rounder particles. Some results in which sulphonated products were trommelled in the presence of water are given in Table 9.[x] They indicate that better attrition indices may be obtained, but there is still some doubt whether a sufficiently low attrition index can be obtained by this process unless the original coal possesses the desirable characteristics.

(d) Type of Coal:

These tests were conducted on two coals having the Grindability Indices shown in Table 10.

[x] In the case of sample L.8 Table 9, trommeling was applied before, sulphonation, no water being added and the -36 mesh material being subsequently removed prior to sulphonation.

TABLE 8.

EFFECT OF DEGREE OF SULPHONATION.

Product Number	L 3	L 5	L 6	L 7	L 4
Sulphonation Tempt.(^{o}C)	145	160	160	160	160
Duration (mins):					
Total	310	125	185	245	310
To app. Saturn.	95	125	125	125	125
SO2 Consumption:					
Total (% of dry coal)	263	292	323	359	394
Yield(% of dry coal):					
Total	133	128	131	133	133
- 36 mesh	12	6	6	8	11
Swelling w. Wetting(%)	9.7	8.6	19.1	28.2	31,2
Capacity (Air dry basis) (grains CaCO3/cu.ft.)	13,300	10,800	12,700	14,700	16,400
Avg. Hardness of Treated water (p.p.m.)	0	0	0	2	3
Chem. Efficiency: (Lb.HCl/Kilograin CaCO3)	0.154	0.190	0.162	0.140	0.125
Attrition Index �	2467	1180	1442	2151	2939

✱ Attrition index of original coal 76 .

TABLE 9.

EFFECT OF TROMMELING ON ZEOLITES.

	Quantity of zeolite used 70 grams. Water 200 c.c. Drum rotating at 140 r.p.m.							See foot-note Page 13
Sample	C Z			L 6				L 8
Trommeling for (hrs.)	0	$\frac{1}{2}$	$1\frac{1}{2}$	0	$\frac{1}{2}$	$1\frac{1}{2}$	$15\frac{1}{2}$	12
- 36 mesh material formed (%)	-	1.1	1.6	-	1,3	2.1	4.1	6.0
Swelling in Water (%)	27.4	0	10.1	19.1	0	12.0	21.0	10.8
Capacity (air dry) (grns CaCO3/ cub.ft.)	16600	12400	13300	12700	11500	11700	12900	10100
Avg. Hardness of treated water (p.p.m.)	4	0	0	0	0	0	1	1
Attrition Index	2977	1483	1395	1442	1202	1100	994	1092

TABLE 10.

GRINDABILITY INDEX % (VOL. BASIS) BY BALL MILL
METHOD (A.S.T.M. STANDARDS 1942 III, P.865.
D 408 - 37 T)

Coal Sample	Index
M	31.7
L	44.4

Results obtained with these coals are given in Table 11.

TABLE 11.

TESTS ON ZEOLITES PREPARED FROM SAMPLES M AND L.

Sample	M			L		
	Orig. Coal	M1		Orig. Coal	L 10	
		Oven dried	Air dried		Oven dried	Air dried
Moisture Content of air dry prod.(Wt.%)	–	13.6	15.3	–	13.0	15.3
Capacity (air dry) (grns CaCO3/cu.ft. zeolite)	–	12200	12900	–	12000	13100
Avg. Hardness of treated water (p.p.m. CaCO3).	–	2	3	–	1	1
Chem. Efficiency (lb.HCl/Kilograin CaCO3)	–	0.168	0.159	–	0.171	0.157
Attrition Index	46	500	626	76	1045	863

The tests indicate that hard coals should be chosen as raw

material for the production of zeolites.

(e) Method of Drying Product:

According to the literature oven drying of zeolites should
be avoided as this affects the hardness and capacity. No detailed
tests have been done and the figures given in Table 11 are not
conclusive.

PREPARATION OF SODIUM ZEOLITE FROM CARBONACEOUS HYDROGEN ZEOLITES.

Since the application of hydrogen zeolites is mainly confined
to large installations under proper control, and there seems to be
a wide field for application of sodium zeolites in small installations,
the conversion of carbonaceous hydrogen zeolites was studied in
greater detail.

It/......

It has been found that the medium in which the zeolite is being treated should not become too strongly alkaline at any stage and therefore the use of reagents such as caustic soda and even sodium carbonate is excluded.

The best results have been obtained when placing the zeolite in sodium chloride solution and carefully neutralising any free acid formed with sodium carbonate. Methyl orange was used as external indicator since the medium was very dark and the zeolite tended to adsorb the indicator. During the treatment the mixture was stirred frequently.

In former tests the sodium zeolites were regenerated with the quantities of sodium chloride recommended by Broderick and Bogard 2), irrespective of their capacity. This is not a desirable procedure. When regenerating sodium zeolites with a quantity of sodium chloride equivalent to the amount of acid used for regeneration in the hydrogen cycle, the zeolite has a higher capacity and the average hardness of the softened water is also improved as indicated by the results given in Table 12 (page 17).

Poorer attrition indices may be obtained when regenerating the zeolite to greater capacity but the other advantages accruing are such that it is considered advisable to work at a 60 - 65% chemical efficiency rather than to under-regenerate.

It has been stipulated in the literature that zeolite [3) and 4)] samples submitted for attrition index tests should be regenerated prior to testing. This stipulation has been made because the condition of the zeolite is probably unknown and it is essential that the comparative attrition index test should be carried out under similar conditions in every respect.

In practice the zeolite is subjected to the highest degree of attrition during back-washing operations of the spent zeolite, prior to regeneration.

The possibility that a sample of zeolite may arrive at the laboratory in a regenerated condition cannot be excluded. In such a case the zeolite would be over-regenerated by applying a standard

TABLE 12.

COMPARISON OF CHARACTERISTICS OF ZEOLITES REGENERATED BY VARYING QUANTITIES OF REGENERATING AGENT.

Sample	Cycle	Conversion to Na Zeolite by	Regenerating Agent and Dosage (grm. equiv./1 Zeolite)	Capacity (grains CaCO3/cu.ft. Zeolite) Air dry	Wet-swollen basis	Avg. Hardness of treated water (ppm. CaCO3)	Chemical Efficiency lb$\left(\frac{HCl}{NaCl}\right)$/K.grain CaCO3 removed.	$\left(\frac{Equiv.(HCl)}{(NaCl)}\right)$ for regeneration (%) / (Equiv. hardness removed)	Attrition Index
CZ	H-cycle	-	0.901 HCl	16,600	13,000	4	0.124	84.2	2977
CZ	Na-cycle	in tube	0.685 NaCl	10,300	8,100	9	0.243	68.8	1906
CZ	Na-cycle	NaCl-Na2CO3	0.685 NaCl	10,700	8,800	12	0.234	71.4	390
CZ	Na-cycle	NaCl-Na2CO3	0.901 NaCl	12,100	10,000	4	0.272	61.4	448
L4	H-cycle	-	0.901 HCl	16,400	12,500	3	0.125	83.2	2939
L4	Na-cycle	in tube	0.685 NaCl	11,500	8,800	12	0.217	76.8	not detd.
L4	Na-cycle	NaCl-Na2CO3	0.685 NaCl	9,600	8,000	11	0.260	64.1	2589
L4	Na-cycle	NaCl-Na2CO3	0.901 NaCl	11,900	9,900	3	0.276	60.4	3061

regeneration procedure before testing, and therefore the procedure does not give a guarantee that all zeolites will be treated under similar conditions.

It is therefore considered that a better procedure would be to subject any zeolite submitted for test to a cycle of operations (using a water of standard hardness) until a constant working capacity value has been obtained, and then determining the attrition index on the spent zeolite at the end of the last cycle. This should not be unnecessarily tedious since a zeolite sample would usually not be tested for attrition index only.

THE RECOVERY OF SO2 FROM SULPHONATION GASES.

Analyses of a number of sulphonated coals revealed that only about 3 - 5% of the SO2 used is actually chemically combined with the coal. Some of the SO2 is converted to sulphuric acid and would not be recoverable as SO2.

In order to establish how much SO2 might be recovered from the gases issuing from the sulphonation retort an experiment was done in which the gas was passed through caustic soda solution. This solution and the sulphonation product were analysed and a SO2 - balance drawn up. The results are given in Table 13.

TABLE 13.

SULPHUR DISTRIBUTION IN PRODUCTS FROM TEST L 5.

	Grams	Wt. % of total SO2 used	Wt. % of SO2 converted to SO3
SO2 used during test (grms)	573	-	-
SO2 converted to SO3 over catalyst	510	89	100
SO2 combined with coal	27	5	5
SO2 as SO3 or H2SO4 in exit gases	83	15	16
H2SO4 retained in retort, and other losses - by difference (as SO2)	146	25	29
SO2 in exit gas from reconversion of SO3	254	44	50
SO2 in exit gas(SO2 not converted to SO3 over catalyst)	63	11	-

Only about half the SO2 used would be recoverable but nevertheless this is a substantial quantity and its recovery would affect the SO2 cost very substantially.

APPLICATION OF ZEOLITES FOR DOMESTIC USE.

Sufficient evidence has been collected in this investigation to be able to state that certain South African coals can be used as raw materials for producing zeolites.

Although it is not possible to determine the cost of production of zeolites from laboratory experiments with any degree of certainty, a general consideration of factors, such as the raw material requirements and their value, suggest that there is every possibility that the material could be sold at a price comparing favourably with that of imported zeolite.

The application of zeolites in industry need not be discussed in detail, since there is quite a volume of literature on the subject [5].

There seems to be a considerable scope for small domestic water treatment installations in South Africa where hard water is very frequently encountered. Here the water softening agent is usually, though / unintentially, the soap used for washing.

A comparison of the cost of soap on the one hand, and of salt required to regenerate a sodium zeolite on the other hand, is interesting.

A cubic foot of sodium zeolite (prepared from coal) should have a capacity of approximately 8000 grains CaCO3 of hardness. It would therefore be able to produce 1000 gallons of soft water per cycle when treating water having a hardness of 116 p.p.m. such as the Pretoria Municipal supply, or 230 gallons of soft water when the raw water has a total hardness of 500 p.p.m.

The zeolite would require $2\frac{1}{4}$ lbs of salt to regenerate it to working capacity, costing 1.8d. at 12/- per 200 lbs. *

In order to determine the cost of soap required to soften the same quantity of water, Sunlight soap was chosen as a typical household soap. An alcoholic solution of this soap containing

1 gram/....

(* Retail Price quoted in Pretoria, Nov., 1944.)

1 gram of soap per 100 c.c. was titrated with "standard" $CaCl_2$ solution having a hardness equivalent to 250 mgrm. $CaCO_3$ per litre. It was determined that 1 gram of soap was equivalent to 1.678 grains of hardness (as $CaCO_3$). Therefore 8000 grains ($CaCO_3$) hardness require 4,770 grams of soap. Since a twin cake of soap weighing 244 grams cost 6d. the 4770 grams would cost 9/9d.

The comparative costs of softening water by soap and by zeolite are therefore about 117 pence and 1.8 pence respectively. The zeolite process would require a special apparatus and a figure for depreciation, interest and wash water for the zeolite after regenerations[*] would have to be added to the 1.8 pence, but this should not alter the comparative cost very appreciably

[*] Wash water requirements are directly proportional to the hardness of the water being softened.

LITERATURE REFERENCES.

1. Beaton, R.H. and Furnas, C.C. Ind. Eng. Chem., 33, 1500-13 (1941)

2. Broderick, S.J. and Bogard, Dale, U.S. Bur. Mines, Repts. Investigations 3559 (1941), and Ind. Eng. Chem., 33, 1291-6 (1941).

3. Broderick, S.J. and Hertzog, E.S."Accelerated Tests for Determination of Attrition Loss of Carbonaceous Zeolites." J. Amer. W.W. Assocn.,·34, 94 (1942).

4. American Water Works Association. "Tentative Manual of Zeolite Test Procedures" (Ion- Exchange Materials – Cation Exchangers Operating on the Sodium Cycle). 2nd. Printing, June, 1943. American Water Works Association, 500 Fifth Avenue, New York 18, N.Y.

5. For Example:

    (a) Fodor, N. The Eng. Jourl. 24, 435-8 (1941).

    (b) Appelbaum, S.B., J. Amer. W.W. Assocn. 30, 946-74 (1938).

    (c) Broderick, S.J. U.S. Bur. Mines, Repts. Investigations 3571 (1941).

    (d) Lindsay, F.K. Ind. Eng. Chem. 35, 378-80 (1943).

    (e) Donnelly, R.P. Colliery Engineering, 20, 122-5 (1943).

    (f) Tiger, H.L. and Sussman, S. Ind. Eng. Chem. 35, 186-92 (1943).

    (g) Rawlings, F.N. and Shafor, R.W. Sugar 37, No. 1, 26-8 (Jan. 1942).

    (h) Benson, R.E. Amer. Chem. Abstract. 36, 4641 (1942).

    (j) Griessbach, R. Angew. Chemie, 52, 215-9 (1939).

    (k) Anon. The Industrial Chemist. 18, 413 (1942).

FIG: I   SULPHONATION   APPARATUS.

SULFONERINGSAPPARAAT