COMMERCIAL UTILIZATION OF GREENSAND AS POTASSIC FERTILIZER AND WATER SOFTENER

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Glauconite, also known as green sand, has been tested with the view to its utilization as a fertilizer and water softening agent. Its samples have also been analysed as described in the paper, and its softening capacity evaluated.

Introduction

The mineral glauconite, commonly known as greensand, is a complex hydrated silicate of ferroso-ferric iron and potassium which usually contains some magnesium and aluminium and approximates to the formula $K_2 (Mg, Fe)_2 Al_6 (Si_4O_{10})_3 (OH)_{12}$.[1]

The mineral varies considerably in chemical composition and specific gravity depending upon its nature of origin and other minerals associated with it.

Greensand is available in the form of deposits in many countries like U.S.A., U.K., France, Western Australia and Belgium and has been used in the neighbourhood of their origin as the source of low grade potassium and phosphorus fertilizer. It has also been employed for removing calcium and magnesium from domestic and industrial water supplies. The softening capacity of the mineral ranges from 2800 to 5000 grains[2] (as $CaCo_3$) per cu. ft. of the material (as against 10,000 grains for the synthetic type zeolites). The effluent may be as low as 5 p.p.m. or less in hardness. The spent sand can readily be regenerated by contact with a concentrated solution of sodium chloride. After thorough washing, the exchanger bed becomes ready to function again as a softening agent.

Large deposits of the mineral have been reported in Chichali Pass area of Kalabagh in the District of Mianwali by the Geological Survey of Pakistan, and several samples have been received by these Laboratories through their courtesy.

Work on these samples has been undertaken to determine the potash contents in different samples and study the feasibility of utilizing this potash as fertilizer. At the same time, the ion exchange capacities of the samples have been thoroughly studied. In all, eight different samples have been examined. The work is divided into two parts, dealing with the availability of potash and ion exchange capacity respectively.

I. Extraction of Potassium

Physical and Chemical Nature of the Samples.—The samples vary in appearance from dark-grey to blackish green colour without any lustre. They are opaque with uneven fracture and have specific gravity ranging from 2.5 to 2.8.

All the eight samples of greensand have been chemically analysed.[4,5] The results are recorded in Table 1. They are essentially silicates of iron and aluminium with total alkali as oxide varying from 2.09 to 6.03%. The useful potassium oxide varies from 1.28 to 4.28%. Determination of phosphorus[6] in 4 of the 8 samples does not show any higher percentage of P_2O_5 than 0.43 and does not warrant them to be useful as phosphorus fertilizers.

All the potassium is not readily available for nutrition of the plants, but only a small fraction of it is in exchangeable form. The results of the determination[3] of available potassium alongwith other bases of the four samples are shown in Table 2.

As most of the potassium is in a combined form and may only be slowly utilized by the plants, when applied as a fertilizer, the cost of transportation of the material becomes a matter of serious concern as several tons have to be applied per acre of land and specially if the land being fertilized lie at a considerable distance from the place of occurence of the mineral. The land in East Pakistan has been reported to be lacking in potash content, a process for extraction of potash from the greensand becomes a necessity. Several experiments have been performed to evolve a method of extraction of potassium using a suitable flux.

Experimental Procedure.—Variable proportions of 100 mesh greensand, mixed with calcium chloride

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TABLE 1.—CHEMICAL ANALYSIS OF GREENSAND.

	Sample 1 %	Sample 2 %	Sample 3 %	Sample 4 %	Sample 5 %	Sample 6 %	Sample 7 %	Sample 8 %
Loss on ignition	8.34	8.83	8.53	10.50	8.50	8.04	7.87	7.81
Silica	51.45	50.15	45.95	42.00	47.45	49.15	52.12	55.02
Ferric oxide	21.80	19.60	26.78	32.04	34.62	29.32	22.30	17.82
Alumina	7.35	10.05	10.08	5.90	4.39	8.12	7.38	10.01
Titanium oxide	0.17	0.30	0.48	0.35	0.12	0.25	0.23	0.15
Calcium oxide	1.54	1.86	1.61	2.57	0.93	1.95	2.58	2.64
Magnesium oxide	2.52	2.74	2.16	2.53	0.79	0.89	1.26	1.55
Potassium oxide	3.56	4.28	2.14	2.50	1.28	1.39	3.58	2.88
Sodium oxide	2.60	1.75	1.85	1.68	1.04	0.70	2.74	2.16
Phosphorus pentoxide	0.27	0.23	0.34	0.43	not done	not done	not done	not done
Total:	99.60	99.79	99.92	100.50	99.12	99.81	100.06	100.04

TABLE 2.—EXCHANGEABLE CATIONS IN GREENSAND.

	Sample 1	Sample 2	Sample 3	Sample 4
Total exchangeable bases as m. eq. per 100 g. of sample	29.4	34.5	29.7	39.1
Exchangeable calcium as m. eq. per 100 g. of sample	25.0	26.0	24.6	31.4
Exchangeable potassium as m. eq. per 100 g. of sample	3.5	3.07	3.46	2.84

and calcium carbonate, are introduced in a graphite crucible and heated in a big muffle furnace at various temperatures for a period of one hour and a half. The reaction product is taken out, cooled, detached from the crucible and powdered. An aliquot portion of the powder, 1 to 5 g., depending on the amount of greensand in the mixture, is taken for the determination of potash. The powder is leached with hot water free from the chloride and potassium determined as potassium perchlorate, the intermediate steps being similar to the method of Lawrence Smith. The results obtained are as follows.

Effect of Temperature.—It has been observed that the extraction of potassium depends greatly on the reaction temperature (Table 3).

It is observed that the optimum temperature for extraction lies between 850° to 900°C. At higher temperatures the extraction is low, presumably because alkali salts are volatile at these temperatures.

Effect on the Variation of Sample Versus Flux.—Although the extraction efficiency of potassium decreases, it will be worthwhile to select the most

TABLE 3.—EFFECT OF TEMPERATURE ON EXTRACTION (GREENSAND: CALCIUM CHLORIDE: CALCIUM CARBONATE 1:1:5).

Reaction temperature	Recovery of K %
600 °C.	51.9
650 °C.	61.7
750 °C.	70.8
800 °C.	90.7
850 °C.-880 °C.	94.6
900 °C.-940 °C.	92.6
1000 °C.-1030 °C.	70.6
1160 °C.-1200 °C.	13.2

TABLE 4.—EFFECT OF VARIATION OF RATIO OF SAMPLE TO FLUX.

Weight of sample g.	Reaction mixture		Recovery of K %
	$CaCl_2$ g.	$CaCO_3$ g.	
10	10	50	91.0
25	10	50	81.4
50	10	50	59.1
75	10	50	38.4
100	10	50	34.6
150	10	50	34.4
200	10	50	16.8

suitable mixture, because it will not only be the cost of greensand which will come into consideration, but the costs of limestone and calcium chloride will play their part too.

Effect on the Variation in the Nature of Flux.—Although calcium carbonate is available as such in the form of calcite, limestone and marble, calcium chloride needs manufacture. The effect of eliminating calcium chloride and its replacement by calcium sulphate which is available in the form of gypsum, has been studied. In the case of heating with only calcium carbonate with requisite proportion of greensand and at required temperature, the recovery of potash was to the extent of 16.1% only. Treatment with calcium sulphate alone yielded only 1.1% potash in the soluble form. A 50% decrease of calcium chloride in our experimental flux also showed considerable decrease in the extraction.

Nature of the Residue after Extraction of Potassium.—It appears that the economic success of extraction of potassium depends on the utilization of large amount of waste material. The chemical analysis of the waste left after leaching of the reaction product of sand: $CaCl_2$: $CaCO_3$ = 2:1:5, shows loss of ignition 17.50%, silica 12.68%, alumina 1.95%, iron oxide 6.38%, calcium oxide 59.95% and magnesium oxide 1.95%. The waste may be utilised for the manufacture of special Portland Cement by adding requisite amount of silica.

II. Exchange Capacity of Greensand

Experimental.—The material is first of all ground and passed through 10 mesh B.S. seive. Finer particles clogs the column and is not suitable. In the samples analysed the clayey matter associated with greensand was from 5 to 45%. The samples are therefore washed repeatedly by decantation with water until reasonably free from suspended matter, and are then dried at 110-120°C.

Filling of Column.—A chromatographic column of 18 mm. diameter and 40 cm. effective length was taken for the purpose. One hundred g. greensand was introduced in the column by wet filling process. The activation of the sand was accomplished by passing a 5% solution of sodium chloride, and then washing thoroughly with water to remove the excess.

Exchange Capacities and Softening of Hard Water.—The exchange capacities of all the samples with respect to calcium was determined by passing a standard solution of calcium chloride prepared from calcium carbonate. Every 25 ml. of the elute was collected and titrated for calcium contents by E.D.T.A., using Eriochrome black T, as indicator. The exchange capacities are shown in Table 7. For camparison, exchange capacities of greensand available elsewhere are also given.

TABLE 5.—EXCHANGE CAPACITIES OF GREENSAND (M. EQ./100 G.).

Sample No.	Capacity	Sample from elsewhere	Capacity
1	17.0	Knaphill	15.0
2	18.6	W. Australia	17.0
3	9.6	New Jersey, U.S.A.	18.0
4	7.5		
5	7.9		
6	10.87		
7	16.7		
8	15.6		

The removal of cations other than calcium was also investigated.

TABLE 6.—EXCHANGE CAPACITY OF GREENSAND SAMPLE NO. 7 FOR DIFFERENT CATIONS.

Cations	Exchange capacity m. eq. per 100 g.
Ca^{++}	16.7
Mg^{++}	16.7
Cu^{++}	14.4
H^{+}	7.2

Conclusion

The potash content of the samples of greensand is rather low and it may not be useful for application as such as fertilizer. Its economic utilization will depend on the successful extraction of potassium and some use of the valuable waste. Further experiments are required to examine the feasibility of making cement or similar building material from the waste.

On the side of water softener, it is felt that the material can immediately be used by industrial concerns. One ton of the sand (2240 lbs.), with exchange capacity of 16 m. eq./100 g., will completely remove the hardness of 7168 gallons oi water with a hardness of 250 p.p.m. calculated as calcium carbonate. The bed can be regenerated and used over and over again.

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