Action of Lime on Greensand^{1,2}

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In the last few years a great deal of work has been done on the extraction of potash from various minerals, such as feldspar, leucite, mine tailings, greensand, etc. For the purpose of liberating the potash, treatment with lime or with a mixture containing lime has been employed rather extensively. This paper gives the results of close study of the action of lime in the presence of water upon greensand or glauconite.

To show the importance of greensand, it may be mentioned that this raw material underlies the surface of hundreds of square miles of the State of New Jersey in beds of commercial value, and within reach of a steam shovel.

The process discussed herein has been in actual operation at a small manufacturing plant for several years, and in its early stages was described by H. W. Charlton.³ In outline, this process as now employed consists in heating a slurry made from 1 part of ground greensand, 1 part of lime, and 5 parts of water or weak washings in a digester for about 1 hr., at a temperature around 470° F., and under sufficient pressure to keep the water in the liquid phase. This will be somewhat over 500 lbs. pressure.

The chief reaction which takes place is that of the lime upon the greensand, which on the one hand liberates the potash in the form of a very pure caustic potash, and on the other hand produces a material high in lime which possesses valuable cementitious and liming properties.

An analysis of greensand that has been commercially used is given herewith:

TYPICAL NEW JERSEY GREENSAND		Per cent
Silica.....	SiO ₂	49.8
Alumina.....	Al ₂ O ₃	9.8
Iron (figured as).....	Fe ₂ O ₃	18.0
Lime.....	CaO	0.9
Magnesia.....	MgO	7.7
Potash.....	K ₂ O	7.4
Soda.....	Na ₂ O	0.4
Sulfuric acid.....	SO ₃	0.24
Phosphoric acid.....	P ₂ O ₅	0.25
Loss on ignition.....	...	5.6
TOTAL		100.1

The action of the lime has been studied from the following aspects:

- 1—Effect of state of division of the greensand (Table I).
- 2—Effect of temperature of digestions (Table II).
- 3—Effect of ratio of water used (Table III).
- 4—Effect of substituting KOH solutions for the water (Table IV).
- 5—Effect of variations in lime used (Table V).
- 6—Effect of addition of various salts (Table VI).

APPARATUS

The method of conducting the experimental work offered various difficulties, and a number of different types of apparatus or digesters were tried. Finally the writer had built a multiple digester somewhat similar to that described by H. D. Gibbs and Max Phillips,⁴ which gave very satisfactory results with a minimum of time and effort. This multiple

¹ Presented before the Division of Industrial and Engineering Chemistry at the 61st Meeting of the American Chemical Society, Rochester, N. Y., April 26 to 29, 1921.

² The work described in this paper has been done in the laboratories of the Eastern Potash Corp., for the improvement of the process to be used at the large plant now under construction at New Brunswick, N. J. This plant will treat 1000 tons of the greensand per day, with about 900 tons of quicklime, and will produce about 65 tons of caustic potash per day, or an equivalent amount of other potash salts, *e. g.*, nitrate. In addition to the potash salts, the plant will turn out several thousand tons per day of a high lime carrying material.

³ THIS JOURNAL, 10 (1918), 6.

⁴ "Alkali Fusions," *Ibid.*, 12 (1920), 145.

digester consisted of a molten metal bath (tin and lead in equal parts) heated by gas burners, and a carriage, so arranged as to revolve in the molten metal. This carriage held six cylinders which were rotated while immersed in this hot metal. The whole moving parts were so arranged that a quick removal could be made in order to take out one or more cylinders for cooling in water and analysis. The individual cylinders measured about 3 in. in diameter by 12 in. long and were similar to those used for shipping nitrous oxide. Each cylinder took a typical charge of:

	Grams
Greensand.....	85
Quicklime.....	85
Water.....	425

The control of temperature was within 5° to 10° F., at around 475° F., which was considered very good; furthermore the initial heating of the cylinders when plunged into the hot metal was rapid, taking only a few minutes.

EXPERIMENTAL DETAILS

In general the experimental work indicated that the most economical yields of potash were obtained by heating under agitation a slurry of

	Parts
Finely ground greensand.....	1.0
Quick lime.....	0.9
Water or weak washings.....	5.0

at a temperature of 470° F., under a pressure of about 550 lbs., for 40 min. In this case about 61 per cent of the potash in the greensand was converted into the soluble form. In the presence of various accelerators, such as nitrates, the conversion was increased to 81 per cent. The details of the experimental work are given in the following tables:

TABLE I—EFFECT OF STATE OF DIVISION OF GREENSAND

EXPT. No.	CONDITION OF GREENSAND	Per cent Potash Converted 40 Min. at 470°–480° F.
B 58	Unground	16.8
B 61	Ground, 90% 200 mesh, calcined	75.6
B 66	Duplicate	72.3
B 67	Unground, calcined	17.5
B 19	Ground, 90% 200 mesh	60 (Av.)
B 21		
B 22		
B 26		

Table I shows the importance of fine grinding, and this is to be expected, as the action of the lime can only be on the surface of the solid particles. Agitation during digestion increases the yields, and violent agitation is very effective; it is, however, not practical to carry this out on a large scale, and we have secured the same result by allowing the digestion to proceed for a somewhat longer interval.

TABLE II—EFFECT OF TEMPERATURE OF DIGESTION

EXPT. No.	Temperature ° F.	Time of Digestion	Per cent Potash Converted
		Medium Temperature	
B 29	400–414	10	26.1
B 28	398–412	40	43.5
B 36	389–397	60	44.2
B 33	398–402	60	56.4
B 32	389–401	120	56.2
B 35	389–398	120	58.8
		High Temperature	
M 19	470–480	20	47.5
M 20	470–480	40	65.3
M 21	470–480	60	68.8
M 22	470–480	90	74.2
M 23	470–480	120	77.9
M 24	470–480	240	83.4

A great many experiments indicated that the yield at 470° to 480° F. was very much higher than at temperatures up to 425° F. The results shown in Table II indicate that the recovery of potash from a digestion of 40 min. at 470° to 480° F. (about 500 lbs. steam pressure) is higher than from a digestion of three times that interval at 390° to 400° F. (about

225 lbs. steam pressure). The digesters for the large-scale plant are accordingly being built to work at 500 lbs. pressure.

TABLE III—EFFECT OF RATIO OF WATER USED

EXPT. No.	Ratio Greensand: Lime: Water	Time of Digestion Minutes	Per cent Potash Converted
B 4	1:1.5	10	57.0
B 9	1:1.6	10	54.4
B 10	1:1.7.5	10	56.5
B 11 ^a	1:1.10	10	60.0
B 11 ^b	1:1.10	10	55.1
B 21	1:1.5	40	59.1
B 20	1:1.6	40	63.9
M 19	1:1.5	20	47.5
M 25	1:1.10	20	58.2
M 20	1:1.5	40	65.3
M 26	1:1.10	40	68.9
M 21	1:1.5	60	68.8
M 27	1:1.10	60	75.1
M 22	1:1.5	90	74.2
M 28	1:1.10	90	76.1
M 23	1:1.5	120	77.9
M 29	1:1.10	120	78.1
M 24	1:1.5	240	83.4
M 30	1:1.10	240	85.6

The most concentrated slurry that can be handled economically is the one with a 1:1:5 ratio of greensand, quicklime, and water. It was of interest to determine whether increase in dilution would sufficiently increase the potash recovery to pay for the handling of the larger amounts of solutions, which, in case of the 1:1:10 ratios shown in Table III, would mean the increase of the primary potash liquor from 5000 to 10,000 tons per 24 hrs. The table shows a slightly greater yield with the doubling of the amount of water, which yield is, however, not increased as much for the longer intervals of digestion as for the first 10 or 20 min. It is more economical to secure the greater recovery by digesting for a longer period than to handle and evaporate the larger bulk of solution.

TABLE IV—EFFECT OF SUBSTITUTING CAUSTIC POTASH SOLUTIONS FOR WATER IN THE 1:1:5 RATIO OF GREENSAND, LIME, AND LIQUID

EXPT. No.	Per cent Strength Caustic Potash Solution Used	Per cent Potash Converted 40 Min. at about 470°-480° F.
B 19	Water	60 (Av.)
B 21		
B 22		
B 26		
B 60	0.5	57.8
B 59	1	58.5
B 48	1	28.3 (?)
B 57	1	47.6
B 49	2	61.9
B 50	3	73.5
B 51	5	61.4
B 52	10	59.6
B 30	20	62.3
M 12	Water	61.7
M 7	0.5	54.8
M 8	1	50.0
M 9	2	49.4
M 10	3	49.6
M 11	10	54.2

The possibility occurred to the writer of dividing the plant in halves, running one-half in series with the other, and thus making the potash liquor of the first half the "make up" liquor for the second half. To determine whether this could be done, the effect was studied of substituting potash liquors of various strength for the water in the slurry. Table IV gives the results and indicates that while there is a noticeable

TABLE V—VARIATIONS IN LIME RATIO AT DIFFERENT DIGESTION PERIODS (All at high temperature of about 470°-480° F.)

EXPT. No.	Ratio Greensand: Quicklime: Water	Equivalent Free CaO Used Grams	CaO in Residue Grams	CaO Consumed Grams	Time Digestion Min.	K ₂ O Converted Per cent
B 40	1:0.5:5	42.5	39.5	0.0	39.5	40
B 39	1:0.6:5	51.0	47.5	0.7	46.8	40
B 38	1:0.75:5	64.0	59.3	11.1	48.4	40
B 37	1:0.9:5	76.5	71.2	21.1	50.1	40
B 43	1:1.5:5	85.0	79.1	23.2	55.9	40
B 47	1:1.5:5	85.0	79.1	29.3	49.8	40
B 42	1:1.25:5	106.3	98.8	41.8	57.0	40
B 41	1:1.5:5	127.5	118.6	57.1	61.5	40
B 45	1:1.5:5	127.5	118.6	64.4	54.2	40
B 53	1:1.5:5	85.0	79.1	17.2	61.9	80
B 55	1:1.5:5	127.5	118.6	49.3	69.3	80
B 54	1:1.5:5	85.0	79.1	14.4	64.7	120
M 6	1:0.6:5	51.0	47.4	0.0	47.4	40
M 5	1:0.75:5	63.75	59.3	11.5	47.8	40
M 4	1:0.8:5	72.25	67.2	16.6	50.6	40
M 3	1:0.9:5	76.5	71.1	21.7	49.4	40
M 2	1:1.5:5	85.0	79.1	29.4	49.7	40
M 1	1:1.25:5	106.25	98.8	43.3	55.5	40

decrease in the potash recovery, yet such caustic potash solutions can be practically substituted for water. The limit to this working of parts of the plant in series is set by the amount of weak washings obtained from the filtration units, which of course must be taken care of in the "make up."

It was difficult to carry out accurate analyses of the experiments listed in Table IV. The liquor could not be analyzed with the accuracy necessary to determine the increment of potash, hence the residue was washed free of soluble potash and the unconverted K₂O determined.

As a saving of 10 per cent of the lime used amounts to 100 tons per day, a careful investigation of the recovery from different ratios of lime was carried out, and the results shown in Table V. In these experiments, after the filtration of the potash liquor, the solid residue was washed with alcohol so as not to dissolve out any of the Ca(OH)₂, and the residue was analyzed for total CaO and for free Ca(OH)₂. For the determination of the free Ca(OH)₂ in the presence of calcium silicates, etc., the very excellent method of W. E. Emley was employed.¹

In the table the results are figured to CaO from the analyses of both the quicklime used and the residue obtained, and the difference indicates the "CaO consumed." In Table V, this value is given in grams, and it is the weight of CaO that reacted with 85 g. of greensand. We concluded from these and other similar results that the ratio of lime to greensand could be cut to 0.9 part and possibly a little lower.

It is a matter of great interest to know just what occurs in such reactions as these. The microscope indicates the presence of calcium monosilicate in the solid residue obtained from the reaction. If all the silica in the 85 g. of greensand used, namely, 42 g., would react to form the monosilicate, there would be required 39 g. of CaO, or double this amount for the dicalcium silicate. The table shows a "consumption" of free CaO of about 50 g. (except where a very large excess of lime was used over a period longer than 1 hr.). Realizing that all the silica may not react, but also that the alumina probably reacts and consumes some lime, it seems likely that the main product of the reaction is calcium monosilicate.

TABLE VI—EFFECT OF ADDITION OF VARIOUS SALTS

(In each experiment a ratio of 1:1:5 was used for the greensand, lime, and water. The temperature of digestion was about 470° to 480° F.)

EXPT. No.	SALT ADDED	Time of Digestion Min.	Per cent Potash Recovered
Several Blank; water only for comparison			
M 37		40	61 (Av.)
M 31		10	64.6
M 32		20	74.3
M 34		40	77.5
M 35	Calcium chloride, 10.0 g.	60	78.7
M 36		90	79.3
		120	80.4
M 49		10	39.7
M 50		20	61.1
M 51	Sodium nitrate, 10.1 g.	30	67.5
M 52		40	80.9
M 53		60	83.9
M 56		3.0 g.	40
M 55		6.0 g.	40
M 58	Potassium nitrate	12.0 g.	40
B 68		12.0 g.	40
B 70		12.0 g.	40
M 57		24.0 g.	40
M 59	Potassium nitrate (with only 0.9 part of lime)	12.0 g.	40
M 60	Potassium nitrate (with only 0.75 part of lime)	12.0 g.	40
B 69	Calcium nitrate	9.8 g.	40
M 41	Sodium sulfate 99 per cent	6.7 g.	40

CONVERSION OF POTASH INTO SALTS

As there is not a market in the United States for the annual production of caustic potash from the proposed plant, we naturally planned for other potassium compounds. The writer approached this problem with the idea of so trans-

¹ Trans. Am. Ceram. Soc., 17 (1915), 720.

forming the caustic potash as to preserve the hydroxyl part of the caustic as well as the potassium. Experiments indicated that the following reactions worked:

A number of other similar reactions were also successfully tried, but these were the two of most interest. After we had worked on the potassium nitrate for some time, we found that during the time of the Crimean War much potassium nitrate was made in a similar fashion, the caustic potash being derived from the liming of wood ashes.

It then occurred to the writer to add the NaNO_3 in the primary digestion charge, and thereby to produce KNO_3 and NaOH directly. This worked very successfully, but the surprising observation was made that the recovery of potash was increased from 61 per cent to 81 per cent. In other words, the presence of the NaNO_3 accelerated the action of the lime on the greensand. This led to an investigation of the action of other salts. The most important of such accelerators are summarized in Table VI. Among other accelerating salts are: sodium chloride, sodium chlorate, sodium phosphate, sodium nitrite, sodium sulfite, sodium acetate, sodium bromide, sodium silicofluoride, sodium fluoride, sodium hypochlorite, etc. Ammonium chloride also acted similarly. Potassium chloride had no effect.

The action of calcium chloride is to produce potassium chloride. This has been previously studied and patented for the Company by H. W. Charlton, who has helped on the other work and has arranged patent protection on the action of the nitrate, etc.

In the use of potassium nitrate in the original charge there is no reaction, but simply an acceleration of the attack of the lime, as the potassium nitrate is recovered and used again. In this case caustic potash is produced.

The apparent explanation of the accelerating action of these salts lies in the fact that they increase the solubility of the Ca(OH)_2 in the water and in the weak caustic solutions.¹

The curves shown in the figure summarize the most important facts brought out in the tables in a comparative manner and they are self-explanatory.

SUMMARY

Tables are given showing the action of lime on greensand under various conditions. To secure economic recovery of the potash the following conditions are indicated:

- 1—Fine grinding; that is, 90 per cent through 200 mesh.
- 2—Digestion at around 470° to 480° F. for 1 hr.

¹ Gmelin-Kraut, "Handbuch der anorganischen Chemie," II, 2, 207.

3—A charge ratio of greensand, quicklime, water and weak caustic solution of 1:0.9:5.

4—Addition of various salts for the purpose of:

- (a) Accelerating the reaction.
- (b) Changing the potassium hydroxide to other potassium compounds.
- (c) Both accelerating and changing to other compounds.

In particular, if caustic potash is desired, potassium nitrate is added as an accelerator; while, if potassium nitrate is wanted as the primary product, sodium nitrate is added to the charge; caustic soda is also produced as a valuable by-product in the latter case.

ACKNOWLEDGMENT

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Platinum Production

Estimates of the production of crude placer platinum in the United States in 1920 give Alaska 27 oz., California 656 oz., Oregon 23 oz., and Washington 8 oz. Refiner reported a production of 41,544 troy oz. of new platinum metals in 1920, of which 36,015 oz. were platinum, 418 oz. iridium, 409 oz. osmiridium, 4309 oz. palladium, and 393 oz. of the minor metals, including rhodium and osmium. This represents a decrease of 3565 oz. compared with the 1919 production. 57,710 oz. of secondary platinum metals were also produced in 1920, representing a decrease of 3806 oz. as compared with 1919. Platinum metals imported for consumption in 1920 included 80,955 oz. of crude platinum and unmanufactured ingots, bars, sheets, etc., of which approximately 58,009 oz. are believed to be refined metal; 4718 oz. of iridium; 4473 oz. of osmiridium; 6944 oz. of palladium; 2675 oz. of the minor metals; and 781 oz. of manufactured platinum ware. This was 32,492 oz. more than in 1919. The consumption of platinum metals in the United States in 1920 was 141,041 oz., of which the jewelers took 57 per cent, the electrical industry 19 per cent, the dental industry 11 per cent, the chemical industry 10 per cent, and miscellaneous uses 3 per cent. The stocks of platinum metals at the end of 1920 amounted to 67,508 oz., which is an increase of 55 per cent as compared with the stocks at the end of 1919.

Reduction of Staff at Helium Plant No. 3

Orders have been issued to reduce the staff at Government Helium Plant No. 3 at Petrolia, Texas, and to place the heavy machinery in stand-by condition for the present. The plant has been operated intermittently on an experimental basis since its erection during the war, and it now seems advisable, in view of extreme lack of funds, to work with a smaller unit while accumulating the data necessary for conversion into an economical operating plant. Plant No. 3 has been drawing on the same supply of gas as the large production plant at Fort Worth operated by the Navy, which is now in operation, and since success is contingent upon a steady flow of gas of fairly uniform composition, Plant No. 3 is to be held in reserve while the Fort Worth plant is being brought up to full-scale steady operation. The Petrolia plant has produced helium of 60 per cent purity and has made repeated runs of considerable duration yielding gas of lower purity, but in view of the expense incurred in reprocessing the gas to bring it to the standard for balloon use the Bureau of Mines has endeavored to obtain first run gas of satisfactory purity. The ultimate purpose of the experiments is to provide a plant which shall furnish helium at a much lower cost than is possible by any known operative system.