ORIGINAL PAPERS

RECOVERY OF POTASH FROM GREENSAND¹

By H. W. CHARLTON

In the original process as developed the material adopted was feldspar, but it was later found that glauconite, commonly called greensand, in many respects possesses marked advantages, although carrying a smaller percentage of potash. It exists in almost unlimited quantities in the Eastern states, particularly in New Jersey, and, unlike feldspar, requires neither blasting nor crushing.

It is an accepted fact that any commercially successful process of liberating potash in rocks, etc., must include a method of profitably employing the residue. In this case a building material is produced and has the advantages of an unlimited market, as well as being a superior product capable of being manufactured at a remarkably reasonable figure.

The method consists in digesting under pressure finely ground greensand with lime and water, thereby obtaining caustic potash of remarkable purity and at the same time converting the residue into a material of value.

The reaction is carried out in large digesters or autoclaves, heated by introducing into the charge high-pressure steam in sufficient quantity to maintain the desired pressure of about 225 lbs. for a period of from 2 to 4 hrs. To conserve the heat, at the completion of each digestion the steam is allowed to escape and be condensed in the greensand-lime-water mixture next to be treated, and the contents of the autoclave, which should have a cream-like appearance, is filtered to separate the dissolved caustic potash from the insoluble residue.

With sufficient lagging the unavoidable heat losses are very moderate, especially as the chemical action requires but little, if any, beyond the heat necessary to raise the temperature of the mass to the reaction point. For this reason the efficiency is largely dependent upon the thoroughness of the heat insulation.

On filtering, the potash appears in the filtrate as potassium hydrate associated with so few impurities that on concentration it may be sold as a high-grade product without further treatment.

Following is an analysis:

	Per cent
K ₂ O.....	77.2
SO ₃	0.90
Cl ₂	0.35
SiO ₂	0.70
Al ₂ O ₃	Free

From the origin of glauconite it would naturally be supposed that the percentage of impurities would be higher and the variety greater than is found to be the case. According to standard works on mineralogy, it is a hydrous potassium iron silicate, but this conclusion was probably based on the simple analytical figures, and there are very strong recent data to show that this is not its true composition. As greensand

is at the present time being carefully investigated, it will very probably be shown to be a potassium iron compound enveloping free silica, but not a silicate. That it is of marine origin is undoubted, and its rich green color is probably due largely, if not entirely, to organic matter with which it is chemically combined.

The solid remaining on the filter, which is the insoluble portion resulting from the digestion, is employed in the manufacture of steam-hardened brick, tile, artificial stone, etc. It acts as a binding or cementing material and is incorporated with high silica sand, as is customary in the manufacture of steam-hardened products, but differs fundamentally in that, whereas lime has always previously been employed as a binding agent, in this case a pre-formed self-cementing hydrous silicate performs this function.

In the past, steam-hardened brick, commonly known as Sand Lime Brick, have not been the success predicted. They are not able to stand the weather without more or less crumbling, and the edges and corners are seldom perfect even in the freshly made brick. This is due primarily to the fact that all the binding power depends on the interaction of lime and sand during steaming, with the resulting formation of a surface coating of calcium silicate which binds the sand particles. If any one of the many factors governing this reaction are overlooked, the brick is faulty. Imperfect slaking of the lime, improper mixing, imperfect steaming, a deficiency or excess of moisture, or dull cornered sand, would each be sufficient in themselves to ruin the product. In fact, every detail has to be rigidly observed and little leeway is permissible.

It is also found that the adhesion between the sand and lime in the pressed but unsteamed brick is slight in every case and that these "green brick" crumble unless handled with the greatest care.

When employing the digestion solids as cementing material these troubles are largely overcome. The pre-formed cementing properties insure an unfailing bond in addition to any chemical action that may take place between the hydrous silicate and the sand during steaming. Any type, such as bank, sea or loamy sand is permissible. Ordinary ground rock will serve the purpose. One of the most convincing proofs of the self-cementing properties of the digestion material is its ability to bond ground limestone, with which there could not be any chemical action.

Sand and the cementing material may be mixed in widely varying proportions ranging from 98 and 2 to 40 and 60. In fact, it is almost true that the process is "fool-proof."

The chemical composition of the autoclave residue depends, of course, on the material treated. With feldspar it is probably a complex calcium aluminum silicate, and with greensand a calcium iron silicate. In both cases it possesses remarkable properties, being to a degree self-cementing but capable of acting,

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when subjected to steam pressure, as a powerful binding agent, cementing sand so firmly that small enclosed quartz pebbles fracture before the bond gives way.

The cementing material resulting from the digestion of feldspar is superior to that from greensand, although the latter possesses sufficient cementing power to meet the most rigid requirements and produces a brick of a pleasing light green shade at a greatly reduced cost.

The feldspar brick are of a marble-like creamy whiteness, entirely devoid of a lifeless milky tint, and have surfaces so smooth that at a distance of a hundred feet they cannot be distinguished from marble.

If colored brick are desired, inorganic pigments may be mixed with the binding material, and if an ochre color is to be produced the coloring matter may be obtained as a by-product in the general process. It is necessary to calcine only a portion of the greensand-lime digestion product, under which treatment it becomes a rich ochre, and add it to either the feldspar or greensand cementing material.

The properties of these brick are best illustrated by tests on samples chosen from the general run by an inspector from the Building Department of New York City. The actual tests were carried out at Columbia University and Pittsburgh Testing Laboratory.

	Feldspar Brick	Required Standard
Crushing Strength, lbs. per sq. in.	9267	2000
Modulus of Rupture, lbs. per sq. in.	1060	450
Average Absorption.....	4.44 per cent	Under 15 per cent

The low absorption may be explained partially at least by the voluminous, easily compressible, water-repellent nature of the bonding material. On being mixed with sand and subjected to the usual high pressure in brick presses it oozes in and completely fills all the interstices between the grains of sand.

Another feature, and in some respects perhaps the most important, is the plastic nature of the binding material which adds a toughness to the brick after compressing and before steaming. This makes possible the handling of the "green brick" without breaking off the corners.

While brick is referred to particularly, it is not intended to convey the impression that this is the only marketable product. The particular advantage of brick is the immense market.

In investigating the various factors governing the yield of potash it was found that a high pressure and a large excess of water were absolutely essential. In treating feldspar it is necessary to use eight times its weight of water, and ten is a fair amount. This necessitated a great deal of evaporation, materially reducing the capacity of the plant and requiring a large outlay for initial heating.

After a series of experiments it was determined by a process of elimination that the alumina was the cause of the trouble, and this naturally could not be removed

in the case of feldspar, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$, as it is an essential element in its composition. The only remedy consisted in the adoption of an alumina-free material, or one in which this element was partially or wholly replaced by a non-injurious one.

Greensand appeared very suitable and was tried. Although its true composition is in doubt, the results in this case were surprisingly satisfactory. It was found that the concentration could be doubled or in fact the water could be reduced to a point where it was just possible to agitate the mixture.

A difficulty that has been met in every process of recovering potash from feldspar is the invariable liberation of soda at the same time. This is always difficult and expensive to separate, and especially so where both alkalis are liberated as hydrates. Theoretically potash feldspar is soda-free, but in practice it invariably contains from 2 to 3 per cent.

Greensand is almost soda-free, which is all the more remarkable from the fact that it is of marine origin, being formed on the ocean bed by the selective absorption of potash from sea water by precipitated colloidal silica and ferric hydroxide.

Another difficulty encountered in applying this process to feldspar is the invariable presence of alumina in the digestion liquors. Efforts to entirely overcome this by adding more lime while reducing the amount do not in any case remove it entirely. In the greensand-lime digestions there is not a trace. This is surprising from the fact that the analysis of greensand always shows a little alumina present probably in adhering clayey matter. It must be present in some combination that this process does not break up. This is extremely fortunate.

Another important feature in the process is the employment of a high temperature and pressure in the digestion. The reactions are not only speeded up, as might be surmised, but are different. This is partially due at least to the production of a chemically active sub-hydrate of lime approximating the formula $CaO \cdot CaO \cdot H_2O$, which is formed at pressures of 200 lbs. and over.

That $CaO \cdot H_2O$ should be partially dehydrated during digestion in a large excess of water, such as an amount equal to ten times the weight of the lime, appears to be paradoxical, but such is the case; and it supplies a plausible explanation of the increased activity of the lime in decomposing the feldspar at pressures above 200 lbs. and corresponding temperatures. It is found that the digestion of feldspar with lime at 150 lbs. pressure for any reasonable length of time scarcely liberates any potash, but above 200 lbs. pressure the reaction is rapid.

Greensand, on the other hand, is less refractory and may be liberated at lower pressures, but it is not advisable to employ them, as the yield is uncertain and the insoluble residue unsatisfactory.

Considered from an economic standpoint, it is believed that it is quite feasible to adapt this process to either greensand or feldspar and, in conjunction with the production of a marketable by-product, to

operate at a profit when selling the potash at pre-war prices. With feldspar, owing to the invariable presence of soda, the mixed hydrate required to be carbonated to effect a separation. The potash is then sold as hydrated carbonate. Carbonating is not necessary in the case of greensand as high-grade caustic potash is obtained in one operation. If potassium chloride is desired it is necessary only to modify the digestion by adding calcium chloride to the original mixture.

It is found in the case of feldspar that the percentage potash content does not give reliable data as to the possible yield, this being dependent on unknown factors pertaining to each individual deposit. Often feldspars that are valueless in pottery manufacture, being weathered and mixed with mica, give the highest yield, in some cases up to 90 per cent, while some very high-grade samples yield as low as 30 per cent.

Greensand contains usually from 6 to 7 per cent K_2O and it may be almost completely recovered, but it is found that 70 to 80 per cent of the total potash is a satisfactory yield after considering such factors as dilution, time of digestion, etc. This means the production of about 100 lbs. of K_2O , and binder material for from twenty to thirty thousand brick from each ton of greensand.

If artificial stone, building blocks, roof, floor or drain tile are manufactured, the resulting amount will vary with the composition and weight of the products. If desired, the digestion material without admixture with sand may be molded in its plastic condition, dried and employed as insulating fire-proof blocks. On the other hand, it is believed that brick have the most extensive market. The fact that the greensand beds are usually overlaid with a high silica sand lessens the cost of manufacture. The overburden, which has to be removed in any case, supplies the necessary sand.

The initial experiments and the commercial development of the process have been made possible by the scientific interest exhibited in the undertaking by Mr. Richmond Levering, who has, himself, borne the great expense entailed in its development.

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TOLUOL BY CRACKING SOLVENT NAPHTHA IN THE PRESENCE OF BLUE GAS

By GUSTAV EGLOFF

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All past estimates of the gallonage of toluol which would be required in this war have been far too low. May not the present estimate of Brigadier-General Crozier of 22,000,000 gallons of toluol¹ required by September, 1918, also be far too low for our war needs?

The cry is toluol, more toluol and more toluol!

One of the fruitful fields for increasing our toluol yield is by stripping carbureted water gas,² coal gas and oil gas, by means of suitable scrubbing towers,

for their toluol content. But, to pass the sorely needed legislation, to change from a candle power to a heat standard will take time, unless the War Department, as a military necessity, commandeers or orders the erection of gas scrubbers in every commercial sized gas plant in this country. But it will take time to build scrubbers for the various gas plants. To quickly add 2,000,000 gallons of toluol to our supply, it is proposed in this communication to suggest the use of water-gas machines to crack solvent naphtha and produce toluol in the presence of blue gas.

It is calculated that there will be produced in the year 1917, 15,000,000 gallons of solvent naphtha from which, in round numbers, 2,000,000 gallons of toluol can be made by cracking solvent naphtha in carbureted water-gas machines. A more than sufficient number of carbureted water-gas machines are already installed throughout the country to more than take care of the cracking of 15,000,000 gallons of solvent naphtha from which 2,000,000 gallons of toluol can be quickly made.

SOLVENT NAPHTHA USED

The solvent naphtha used in the following experiment was derived from the thermal decomposition of coal and analyzed, using a standard Engler flask for distillation and the Westphal balance for specific gravity.

DISTILLATION ANALYSIS

Specific Gravity 0.867/15.5° C.

Temp. ° C.	Per cent by Vol.
135.5	1st drop
140.0	49.0
150.0	87.0
160.0	91.5
170.0	96.3
180.0	98.5
183.5	Dry point

CRACKING TEST

The following test of cracking solvent naphtha was conducted upon a Lowe 6' carbureted water-gas set, over a period of 48 hrs. The operation of the plant in cracking solvent naphtha in the presence of blue gas for toluol is practically the same as when cracking gas oil in ordinary carbureted water-gas making, with the exception that the gallonage per hour of solvent naphtha into the cracking zone is higher. The data upon a 24-hr. basis averaged as follows for a carbureted water-gas set:

Make per 6' set per day of gas formed.....	500,000 cu. ft.
Candle power of the gas.....	21 at 21° C.
Candle power of gas per gallon of oil.....	1.75 at 21° C.
Solvent naphtha cracked per 1,000 cu. ft. of gas formed....	12.0 gal.
Gas per gallon of solvent naphtha cracked.....	83.3 cu. ft.
Coke used per 1,000 cu. ft. gas.....	46.0 lbs.
Steam used per 1,000 cu. ft. gas.....	38.0 lbs.
Temperature of superheater base.....	825° C.
Temperature of condenser outlet.....	15.5° C.
Length of run.....	4 min.
Length of blow.....	4 min.
Rate per hour solvent naphtha.....	250 gal.
Rate actual flow of solvent naphtha into system.....	500 gal.
Total gallonage of solvent naphtha passing through set in 24-hr. day.....	6,000 gal.
Light oils collected in drips and seals.....	57 per cent
Tar in gas holder.....	15 per cent

ANALYSIS OF LIGHT OIL

The light oil was distilled in a one-barrel still with steam to a temperature of 170° C. This cut was

¹ THIS JOURNAL, 9 (1917), 1002.

² *Met. and Chem. Eng.*, 16 (1917), 492; Moore and Egloff, *Ibid.*, 17 (1917), 297.