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L A K E C A M P I O N (W.A) A L U N I T E

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G.H. P A Y N E, B.Sc., A.W.A.S.M., A.A.C.I.

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1. GENERAL.

1. THE POTASH POSITION IN AUSTRALIA:

The use of potash fertilizers in this country is of the greatest importance in the growing of sugar, but considerable quantities are also required for the tobacco, potato, tomato, maize, pineapple and banana industries.

Prior to the outbreak of war, there were several kinds of potash fertilizers on the market, imported mainly from Germany, Palestine and France. The most common forms were the chloride and sulphate, with lesser quantities of Kainit, a magnesium potassium compound occurring naturally in the Stassfurt deposits of Germany. The tonnage of potassium salts imported into Australia during the year 1938-39 was 11,155 valued at £126,336. The imports of the chloride and sulphate for the years 1937-38 and 1938-39, together with the country of origin, are shown in Table I.

Table I. Australian Imports of Potash.

Country of Origin	1937-38		1938-39	
	Sulphate	Chloride	Sulphate	Chloride
Palestine	50	3760	635	3989
Belgium	-	-	10	-
France	783	1922	566	1028
Germany	2635	1465	1724	2993
United Kingdom	-	-	-	10
Total	3468	7147	2935	8020

We cannot continue indefinitely to draw on the reserves present in the soil for the potash required by the various crops and in this respect the production of a certain tonnage of these salts locally and without delay becomes imperative to the immediate future of the sugar industry of Queensland in particular.

Economically, the position as regards potash supplies is very different from that obtaining during the last war when the price of potassium sulphate rose from about £8. per ton to £70. per ton in Australia. Then there was a world-wide shortage when German supplies were cut off, but nowadays the United States produces a large proportion of its own requirements and the Palestine development has reached the stage at which considerable amounts could be exported if shipping were available.

A great variety of methods have from time to time been proposed for the extraction of potash from potential raw materials, among which are alunite, leucite, greensand, feldspar, shale, brines, kelp, industrial by-products, cement kiln and blast-furnace fumes, distillery waste and wool-scouring. Many of these sources were successfully exploited in the United States of America during and immediately after the Great War, when European supplies were not available. With the first approach of normal prices again, treatment of all but three of these raw materials was found to be unprofitable. The three exceptions

were brines from Searles Lake (Calif.), distillery waste and cement kiln fume, of which the former is by far the most important. The potash recovered from these sources in U.S.A. supplemented that recovered from the mining of sylvite, sylvinite and polyhalite. 1 first

It is of interest to note here that experiments carried out in Europe and America during the last decade have indicated the technical feasibility of the production of potash fertilizers by blast-furnace smelting of such widely distributed sources as leucite and the potash feldspars; and also the commercial possibilities of producing a concentrated combined potash-phosphate fertilizer by smelting a mixture of raw materials not otherwise available for recovery of their valuable constituents. Production of artificial fertilizers by blast-furnace processes is fully discussed in a bulletin [1] published in 1937 by the United States Department of Agriculture.

In Australia, sources of potash salts, other than alunite, have been investigated to a certain extent. A small tonnage is believed to have been recovered from flue dusts from cement works in Victoria, while in South Australia the exploitation for this purpose of the seaweed *Posidonia australis* has received some attention. The ash of this weed contains about 5% potash and its recovery seems to be an economic rather than technical problem.

Potassium carbonate can be recovered from wool scouring liquors and it is understood that at least one of the scouring companies is considering its recovery from this source. It has been estimated that 2% of the weight of the annual Australian clip of 1,000,000,000 pounds could be recovered as potassium carbonate. Assuming that 5% of the clip is scoured in Australia, this would mean that there is available some 500 short tons of the carbonate annually if it could be obtained at a satisfactory cost. Here again, the process has been shown to be technically feasible, with the main problem being one of economics and mill organisation.

In addition to crude fertilizer potash, there is a limited but vital demand in this country for quantities of the pure salts, in particular the chlorate, chloride and carbonate.

The development of a potash industry in Australia seems then, to be a question of national importance and in this respect, the large alunite deposit of Lake Campion is worthy of special attention. No mining difficulties are involved, there is sufficient material to supply Australia's potash requirements at the present rate of consumption for the next hundred years and, in addition, there are the potentialities of the deposit as a source of supply of alumina, sulphuric acid and sodium salts.

It was towards these ends that the present investigational work was initiated, and this report deals with the first of the above aspects, namely the recovery of fertilizer potash from the alunite of the deposit. It may well prove later that the value of the work lies more in the preparation of a residue suitable for treatment for the recovery of a pure alumina, and indirectly of the strategically important metallic aluminium, than in the recovery of the potash content of the ore. There is no doubt, however, that the successful recovery of the potash would be a big economic factor in the establishment of the proposed alumina industry. This latter industry would be of added value in the light of the relatively poor bauxite deposits known to exist in this country.

2. PROPERTIES OF ALUNITE:

Alunite is a naturally occurring hydrated basic potassium aluminium sulphate having an empirical formula of $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$. It is most commonly associated with acid volcanic rocks where the rock has been largely altered and alunite formed owing to the presence of sulphuric acid solutions or vapours.

The mineral occurs as rhombic hexagonal crystals, with a specific gravity of 2.58 to 2.75 and a hardness between 3.5 and 4.0. The crystals are brittle, transparent to sub-translucent, and optically positive.

Potash alunite is isomorphous with natro-alunite, a complete series of minerals being known ranging from pure $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$ to pure $Na_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$. The composition of pure potash alunite, or simply alunite as it will henceforth be designated, is as follows:-

K_2O	11.4%
Al_2O_3	37.0%
SO_3	38.6%
H_2O	13.0%

The chemical behaviour of alunite under various conditions has been studied by a number of investigators.

The reactions occurring during calcination of the mineral taken from United States deposits have been reported by Waggaman and Cullen [2] and later by Fink, Van Horn and Pazour [3], Ogburn and Stere [4] and Adams [5]. These writers also fully discuss the solubility in acids, alkalies and water of the material at different stages of thermal decomposition. Similar work was carried out on ore from the Pingyang deposits by King and Hsiao [6].

Deposits of alunite are known at Kanowna, near Kalgoorlie, and detailed work on the properties of the mineral from this source was undertaken by Bowley [7] in 1920. He concentrated mainly on its thermal decomposition and its solubility in various reagents. The first of these properties is of outstanding importance in the work on Lake Campion alunite described in this thesis and it is therefore of interest here to list Bowley's conclusions in that direction. His conclusions which agreed in most essential details with those of the other authorities cited above, were briefly as follows:-

- "(i) Alunite is unaffected by dry heat at temperatures up to $300^{\circ}C$.
- (ii) The decomposition of the mineral in alum roasting is in two stages. At $400^{\circ}C$. the mineral loses $4\frac{1}{2}$ molecules of water with the formation of a basic sulphate of aluminium and potash, and on further heating to a temperature of $500^{\circ}C$., the remaining water is removed, forming an anhydrous basic sulphate. On the addition of water the basic sulphates dissociate, producing a true alum and precipitating aluminium hydrate.
- (iii) Alunite heated to a temperature of $800^{\circ}C$. dissociates completely into potassium sulphate, alumina, sulphur

trioxide and water. Part of the sulphur trioxide dissociates further into a mixture of sulphur dioxide and oxygen.

- (iv) On heating alunite to a temperature of 960 C., the potassium sulphate formed is dissociated and interacts with the alumina to form soluble potassium aluminate, or, in the presence of silica, insoluble potassium aluminosilicates."

3. PREVIOUS WORK ON ALUNITE:

Alunite is known to occur widely distributed throughout the world, but the most extensive overseas deposits are at La Tolfa and Montioni in Italy, Musaz and Bereghsasz in Hungary, Marysville in Utah and throughout China and Korea, while lesser deposits exist in France, Austria, Greece, Spain, Nevada and Arizona.

The mineral has been exploited in Italy since the 15th Century for the manufacture of potassium alum, and, according to Thorpe [8] the harder and more compact varieties from Hungary have been used in the past as millstones. The mineral has been used directly as an artificial fertilizer but in more recent years alunite deposits have been worked chiefly for the recovery of potash and aluminium salts, with sulphuric acid as a by-product. The most recent development in this direction, however, is the claim by Eichelberger [9] that commercial production of metallic aluminium from the Marysville alunite will begin in 1942 with an estimated daily output of 50 tons of aluminium ingot.

A considerable amount of investigational work has been carried out on a number of the deposits but the literature on the subject is not very extensive. A large number of claims have, however, been made in the patent literature relative to treatment methods stated to be satisfactory for the handling of these ores.

In the following brief review of the literature, no claim is made to completeness, but the notes will at least indicate the variety of angles from which the alunite problem has been attacked. While some of the methods are commercially feasible, others can scarcely hope for application outside the laboratory.

The calcination or fusion of mixtures of alunite with a wide range of other reagents has been subjected to many investigations in the past. Fox [10] for instance, claims that decomposition of the alunite is facilitated by calcination at a low red heat in the presence of fluorspar while Meyers [11] recommends the calcination of a mixture of alunite and limestone below fusion temperatures. He claims that K_2O and SO_3 are volatilized, while the sinter remaining makes a marketable alumina cement. Simple water-leaching of the calcine obtained by roasting alunite and lime is stated by Morgan [12] to give a good recovery of K_2SO_4 , but in actual practice this method received something of a setback when applied commercially to the Utah deposits during the last war. The operator concerned had shipped some tons of the crystals, obtained by evaporation of the extract, before realising that this "potassium sulphate" was in reality syngenite, the double potassium calcium sulphate $K_2SO_4 \cdot CaSO_4 \cdot H_2O$.

Glaeser [13] heated alunite with steam and $CaCl_2$ at 700°-800°C. to produce HCl, recovering the potash as KCl by leaching the calcine.

Kametzki and Kashcheev [14] calcined a mixture of alunite and ammonium sulphate at 400°-500°C. and recovered the values by water extraction. A similar calcination has been suggested in Australia, with alunite replaced by bauxite,

for the recovery of alumina from the low grade bauxites of this country.

A method which received limited commercial application during the 1914-18 war period was that designed by Cameron and Cullen [15]. A company exploiting the Marysville deposits of Utah used the process which involved roasting ground alunite mixed with sulphuric acid. On leaching the calcine a solution was obtained of alum and aluminium sulphate. Ammonia liquor from a nearby gasworks was used to convert the aluminium sulphate to ammonium alum and the alums were marketed as such.

Shoeld [16] obtained potash alum and $\text{Al}_2(\text{SO}_4)_3$ by treatment with H_2SO_4 of the calcine resulting from ignition of ground alunite and carbon in a reducing atmosphere, while Chow, Liu and Sun [17] extracted nearly 100% of the K_2O by heating a mixture of alunite plus 12% of coke to 800°C . in an electric furnace. When the evolution of SO_2 was complete, the roast was cooled and extracted with water. Potash was recovered from the filtrate while the residue was fluxed with Na_2CO_3 at 900°C . for recovery of Al_2O_3 . Recoveries of SO_2 , Al_2O_3 and K_2O by this method are claimed as 87%, 80% and 100%, respectively. The same workers [18] obtained 96% of the potash as K_2SO_4 by boiling calcined alunite with K_2CO_3 solution.

Work on different alkali fusions has been carried out by Huffman and Cameron [19] in recent years. They found that after fusion with hydroxides of either sodium or potassium, the material was water soluble, and the values could be converted to the corresponding carbonates with precipitation of sulphates by treating the solution with BaCO_3 and CO_2 under pressure. The components were also rendered water soluble by fusion with Na_2S , accomplished by heating the alunite with Na_2SO_4 and coal breeze. Two years later [20] these workers report that the use of K_2SO_4 instead of Na_2SO_4 for the sulphide fusion had distinct advantages, mainly in the recovery of pure potassium salts not readily obtainable when sodium sulphate was used.

They then recommended [21] the sintering of alunite with K_2SO_4 , K_2CO_3 and coal in alundum-lined furnaces, the sinter being leached to obtain a solution containing principally potassium aluminate, K_2SO_4 and K_2CO_3 . After precipitation of a pure alumina, the mother liquor was evaporated to give a practically quantitative recovery of K_2SO_4 . The residue of carbonate with water was used in further alunite decomposition.

Whether the above methods of alkali fusion would apply equally well to run-of-mine ore as to the small high grade samples used in the test work is a point still to be investigated.

Koster, Knickerbocker, Fox and Perry [22] detail a method whereby K_2SO_4 and Al_2O_3 are recovered from alunite by fusion with boric acid. The process involves sintering the alunite with boric acid, leaching the sinter with water to remove the potash and excess boric oxide which are later separated by brine flotation. Al_2O_3 is recovered by sulphuric acid leaching of the water-insoluble residue from the sinter and is precipitated electrolytically from the $\text{Al}_2(\text{SO}_4)_3$ solution. The method requires a mixture of boric acid and alunite containing 30% boric acid and a temperature of 1100°C . for 2 hours.

Knickerbocker and Koster [23] have made laboratory studies of a number of electrometallurgical treatments of alunite. They found, inter alia, that 90% of the Al_2O_3 in high-silica alunite can be volatilized by treatment with chlorine gas and carbon at temperatures of 500° to 625°C . Most of the potash was rendered water soluble and could be leached from the residue and fume.

The possibilities of calcining alunite mixed with no other reagents has, of course, occupied the attention of many workers in this field.

Simple calcination and water extraction has proved applicable in certain instances, while in others either acid or alkaline solutions have been found best as extraction media.

According to Chappell [24] when calcining alunite in either a stack or rotary kiln the formation of aluminates is encouraged by a deficiency of air. Though Hershman and Cooke [25] deliberately maintained reducing conditions within the kiln to obtain these aluminates, the vast majority of workers have calcined under conditions of excess air.

For the majority of calcinations on any but laboratory scales the rotary furnace has been most favoured. The only references found to other means of roasting were in patents taken out by Chappel [26] and [27] in which he suggests the calcination of high grade alunite at 900° to 1000°C . in muffle furnaces to recover an SO_2 uncontaminated with furnace gases. The same investigator [28] also covers a process involving the calcination of the ore in a closed retort and the recovery of elemental sulphur as a sublimation product.

Labutin and Kotypin [29] extracted potash by treating alunite calcined at 550°C . with 5% NH_4OH solution and filtering. The residue was digested with NaOH at 95° - 100°C . whereby 85% of the alumina was recovered as a product carrying 0.5% SiO_2 . Hohorst and Wang [30] recovered 96% of the K_2O by a similar method, during which they found that an excess of NH_4OH led to dissolution of some of the Al_2O_3 . They later [31] treated the potash residue with NaOH at 80°C ., dissolving more than 93% of the Al_2O_3 . This solution they claimed to be suitable for Al_2O_3 recovery by the Bayer process (stirring after seeding), giving a 70-77% yield, the product being practically free from iron and sufficiently low in SiO_2 for metallurgical purposes.

Sun [32], as a step towards obtaining a pure Al_2O_3 from siliceous and ferruginous Chinese alunite, calcined the material at 550° - 600°C . for 4 hours and treated the cold residue at 40°C . for 4 hours with ten times its weight of 6% NH_4OH . The mixture of ammonium and potassium sulphates obtained on evaporation of the extract gave a product suitable for direct use as a fertilizer or for separation into its component salts. This latter step was carried out by Liu [33] by treatment with CaO of a solution of the salts whereby NH_3 is evolved, CaSO_4 precipitated and K_2SO_4 recovered by evaporation. Chow [34] calcined alunite at 575°C ., mixed the calcine with 60% of its equivalent weight of CaO , boiled with water and recovered as high as 95.5% of the K_2SO_4 by concentration of the filtrate.

Tanaka [35] and [36] roasted Korean alunite at 600°C . and extracted with ammonia to recover potash. The residue of Al_2O_3 plus gangue was pulped with water, treated with SO_2 and an aluminium sulphite obtained free from SiO_2 and Fe_2O_3 . This method for the production of a high grade alumina was also found successful by Chow [37].

Yamazaki and Furukawa [38] describe a method in which alunite is ignited at 550° pulped with water and subjected to a stream of SO_2 resulting in solution of 90% of the alunite. Ammonium sulphite is added and at 110°C . over 94% of the Al_2O_3 is precipitated. On filtering, potassium and ammonium sulphates are recovered from the filtrate. After igniting as above, Yamazaki [39] also claims a high recovery of Al_2O_3 and K_2O by treatment with 50.9° Bé H_2SO_4 followed by addition of $(\text{NH}_4)_2\text{SO}_4$ sufficient to convert all the aluminium to ammonium alum. Alumina is recovered subsequently by precipitation with NH_3 from alum solutions.

Other patents covering procedures involving calcination include those of Tone [40] and Hirota [41]. Tone reduces alunite by fusion in an electric furnace at 2100°C . to alumina for the refractory industry, while recovering SO_3 and K_2O as volatilization products. Hirota electrolyses an HCl extract of calcined alunite in a two-compartment cell. Free acid is generated in one compartment while at the cathode $\text{Al}(\text{OH})_3$ is precipitated by the alkali hydroxide generated in the second compartment.

Not as much work has been done on treatment methods not involving calcination. Of these so-called wet methods, treatment of the raw ore with caustic solutions are the only ones to receive much attention.

The behaviour of alunite when treated with KOH solutions under a large number of varying conditions has been studied in detail by Hohorst and Hon [42] and by Adams [5]. The latter obtained 25% of the alumina in solution by treatment with 5N KOH and NaOH , whereas Hohorst and Hon obtained, under optimum conditions, 97.6% of the Al_2O_3 , 99.2% of the SO_3 and 96% of the K_2O in solution by treatment with 12N KOH at 80°C ., with 97% of the alumina going into solution at 40°C . The alumina carried 1.2% of SiO_2 , though this figure was later [43] reduced to 0.3% SiO_2 .

Raw alunite was treated by Wildman [44] with KOH and the $\text{Al}(\text{OH})_3$ was precipitated from the extract by CO_2 . After removal of the $\text{Al}(\text{OH})_3$, potassium sulphate was recovered by evaporation and the mother liquor treated with CaO for regeneration of KOH . Yonemura and others [45] on the other hand, digested alunite with KOH under conditions which gave a solution yielding K_2SO_4 on cooling while the mother liquor, on dilution and seeding, gave a precipitate of aluminium hydroxide.

Detweiler [46] patented a process which involved digestion of raw alunite with boiling HNO_3 . Alumina was precipitated from the extract with NH_3 and KNO_3 recovered from the filtrate.

The economics of potash recovery from alunite as applied to American conditions are discussed fully by Thoenen [47] while in a more recent paper [48] the same writer reviews the alunite deposits of the United States and their possibilities as a source of metallic aluminium.

4. ALUNITE IN AUSTRALIA:

No deposits of any significance are known in Tasmania, Victoria or Queensland.

Larger deposits have been described at Bullahdelah (N.S.W.) and at Carrickalinga and Warnertown in South Australia. In all of these localities the alunite occurs as a lode formation. The three deposits are described by Pitman [49] and Jack [50] in publications of the appropriate State Department of Mines.

The extent of the exploitation of the Bullahdelah ore up to the end of 1927 is summarized by Harper [51] while in more recent years the deposit has been re-opened and alunite shipped for the production in Victoria of potash alum. The South Australian alunite has been developed only spasmodically, the main activity apparently having been during the war years of 1914-18 when some tons of a very pure product were shipped from the Carrickalinga deposit to chemical works in England. Janes [52] states that during the same period Carrickalinga alunite was calcined with limestone in lime kilns and the resulting product, containing 2.5% of potash, used in a small way as a fertilizer.

In Western Australia, deposits have been described by Simpson [53] at Kanowna, Wallangie, Northampton and Ravensthorpe. At Kanowna a minor industry was established during the war years for the winning of a small tonnage of untreated raw ore, which was used as a fertilizer after the addition of 200 lb. of slaked lime per ton of alunite. This addition of lime was claimed to render the K_2O water-soluble, making the mixture a satisfactory substitute for the normal potash fertilizer.

As far as can be ascertained from the published literature no systematic work, other than that carried out by Janes [54] has been undertaken on the treatment of the New South Wales and South Australian alunites. Janes' detailed experiments led him to the conclusion that "the problem is not a chemical or mechanical one so much as an economic one. With favourable conditions Australia should be easily able to supply her needs of potash salts without delay from her deposits of the mineral alunite." He claims that a satisfactory potash fertilizer could be obtained from the alunite of the New South Wales and South Australian deposits by a process involving crushing to about $\frac{1}{4}$ inch, roasting "in a suitable furnace" alone, or, preferably, after the addition of molasses or sawdust, till all soluble alumina is absent and grinding the calcine to minus 40 mesh. The calcine to be extracted with hot water, filtered in a pressure filter and the filtrate evaporated to obtain potassium sulphate. The addition of the carbonaceous material to the alunite prior to thermal treatment was to assist the removal of the SO_3 from immediate contact with the ore by providing other gases produced from the combustion of the admixed material.

The Kanowna (W.A.) alunite has been studied by Bowley [7] whose work led to the conclusions already quoted, but otherwise no systematic work appears to have been carried out on other alunite deposits of this State.

11. THE LAKE CAMPION DEPOSIT

1. LOCALITY:

The deposit is situated at Lake Campion in the Avon district of Western Australia and lies about 22 miles from Burracoppin in a direction a few degrees west of north. It is 7 miles south of the nearest railway siding of Weira which is on the line from Southern Cross via Bullfinch to Wyalkatchem and is some 30 miles north of Merredin on the main Kalgoorlie-Perth road. It is about 165 miles from Perth in a direction 20 degrees north of east.

The district is decidedly dry with an average annual rainfall of only 10 inches and is largely dependent for water upon the nearest standpipe of the Mundaring-Kalgoorlie water supply scheme. At present this branch pipe-line is located about 3 miles from the lake but could readily be extended should a treatment plant be established at the site of the deposit. The evaporation is stated to be 85 inches per annum.

The surrounding country is fairly thickly timbered and could possibly provide sufficient fuel for the generation of producer gas which could be used for roasting and as a source of power if necessary.

2. EXTENT AND NATURE OF THE DEPOSIT:

Lake Campion covers an area of 426 acres and is dry for the greater part of the year. After heavy rains a few inches of surface water may accumulate and remain for several weeks. Permanent water occurs a few feet below the surface, its actual level varying with the season. This water is strongly saline and contains a small percentage of free acid.

Varying estimates of the quantity of ore available have been made, a typical and average figure being 9 million cubic yards of material averaging 60% alunite. It has been found in the laboratory that the density of the ore in situ is approximately 2, thus the above is equivalent to about 8 million tons of pure alunite.

Unlike other Australian alunite deposits, the alunite of Lake Campion occurs as a sedimentary deposit, consisting of very fine material mixed with kaolin and quartz. Except for the first few inches of the deposit where gypsum crystals occur plentifully, and for isolated patches where quartz sand is encountered, the whole of the material readily passes a 200 mesh I.M.M. screen.

A large area of the lake was bored and sampled by a party including the writer. Though some bore holes were taken to a depth of 14 feet, those for sampling were limited to the first $3\frac{1}{2}$ feet, this depth representing some years' supply to a plant of the proposed capacity.

Samples were taken of the first six inches and of each succeeding foot to a depth of $3\frac{1}{2}$ feet. The samples were analysed at the University and except for a few bores near the edge of the lake showed a remarkable consistency with depth and over the area bored. The average K_2O figure was 7.35% equivalent to 64.6% alunite, while silica averaged 21.1%.

Gypsum occurs in varying amounts on the surface and throughout the first few inches but is generally absent below 6 inches. For the first two to four feet the alunite occurs as a dark greyish blue material and with depth this grades through various greys to almost white. Occasional layers of red are

encountered, these usually overlying shallow strata of gritty sand just above bedrock.

3. GEOLOGY OF DEPOSIT:

Lake Campion is one of a salt lake system which appears to have been at an early stage, an old river system running westward to the sea. The salt lakes are divided from each other by ridges of kopai, and occasionally of impure to pure white seed gypsum. These ridges rise to a height of 20 to 25 feet above the level of the lake beds.

Rock outcrops in the vicinity are not numerous, and what there are are usually obscured by laterites of mainly granitic origin. The granites that occasionally outcrop near the lake are distinctly gneissic in character and are typical of those gneissic granites found forming a large portion of the West Australian plateau.

The main rock outcrop actually adjoining the lake occurs at its north-western corner. The rock is a highly altered and decomposed granite in which the feldspars are almost completely kaolinised. The general contours of the land in the immediate vicinity of this outcrop make it the logical choice for the site of the proposed treatment plant.

The lowest layers of the deposit consist of hard red gravel, often formed with conglomerates by siliceous cementing. The whole lies in a depression in the gneissic granite typical of the surrounding country and which undoubtedly forms the ultimate fundamental bed of the lake.

Samples of ore taken from Lake Campion were submitted to Dr. F. Stillwell of the Melbourne University for examination. He divided the samples into a decantation product and a residue by an arbitrary water classification. The decantation product consisted mainly of alunite grains 2 to 5 microns in diameter, with quartz grains ranging in size from 14 to 20 microns present in varying amounts. Occasional grains of bleached biotite and limonite were also reported with abundant limonite accompanying the quartz in samples from the red strata. Some diatom skeletons were present in samples from nearest the surface.

In the classification residues, the chief mineral present was quartz ranging from 3000 to 50 microns in size. Very occasional crystals of pyroxene were detected, together with bleached biotite and grains of limonite. A few needles of gypsum were observed.

An X-ray examination of the material by Mr. J. Shearer of the Physics Department of the W.A. University showed the presence of alunite and quartz, a small quantity of kaolinite and traces of mica, gypsum and dehydrated alum.

4. CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF ORE:

The specific gravity of a typical sample of the dry ore after washing was found to be 2.63, while the water-soluble salts present in the unwashed ore comprised 4.88% of the weight of the sample.

Bowley has made a complete analysis of a sample of the water washed material dried at 105°C. The sample was taken over the first 3 feet of the deposit, and can be regarded as reasonably typical of the deposit as a whole. The figures obtained were as follows:

K ₂ O	7.24 per cent
Al ₂ O ₃	27.47
SO ₃	26.47
SiO ₂	21.17
Fe ₂ O ₃	2.27
CaO	Nil
MgO	0.47
Na ₂ O	0.78
P ₂ O ₅	0.17
TiO ₂	0.12
Cl	0.98
Combined water	12.43
CO ₂	Nil
Organic matter	<u>0.58</u>
	100.15
Less O = Cl	<u>0.22</u>
	<u>99.93</u>

Assuming all the potash to be present as alunite, the above analysis gives an alunite percentage of 63.7, which is in fair agreement with the average figure of 64.6% as obtained on the unwashed bore hole samples taken by the writer and party as mentioned in II.2. The average silica content as shown by analyses of these unwashed samples was 21.1%.

A sample of the sub-surface water, taken during December from a bore hole near the centre of the deposit, had a pH of 4.2 and a specific gravity at 24°C. of 1.069. A complete analysis of the salt content of the water was carried out and the radicals were combined to give their simplest salts with the results shown in Table 2.

Table 2. Analysis of Sub-surface Water:

Salt	Grams per litre	Grains per gallon
CaSO ₄	2.57	180
CaCl ₂	3.96	277
MgCl ₂	10.53	737
Al ₂ (SO ₄) ₃	1.71	120
K ₂ SO ₄	1.04	73
NaCl	70.61	4943
Total Solids	90.42	6330

This is not a good way to record the analysis of a solution of electrolytes. The radicals (anions) should be recorded as gms/litre and as equivalents/litre so that the balance of + and - can be seen. As given, the results are not uniformly selected.

It is evident that the salts from this water are going to represent a considerable percentage of the final recovery of water-soluble salts from the ore.

111. TREATMENT METHODS

Of the large number of treatment methods proposed in the literature, only a few can be considered relative to their application to the Lake Campion deposit.

The suitability of the more recent American methods involving fusion with alkali sulphides, alkalies, or boric acid depends largely on the ready availability of the necessary reagents. In the case of the Maryvale deposits, for instance, sodium sulphate is readily available from the Great Salt Lake and in nearby deposits of Glauber's salts, so that, with a plentiful supply of cheap coal on hand for reduction purposes, the treatment method involving fusion with alkali sulphides takes on some commercial significance. Similarly, large and relatively cheap supplies of borates are available from the Searle's Lake brines of the neighbouring State of California.

In Australia, and at Campion in particular, these favourable conditions do not hold. Methods depending on the use of ammonium salts for decomposition are similarly not favoured, due to the small quantities of these salts available locally and the high freight charges involved in shipping the reagent from gas works in the Eastern States.

In the case of Lake Campion then, and in view of the urgency for producing a potash fertilizer, simple straightforward calcination and water leaching seems the logical method on which to concentrate research work, even though it might involve the production of a relatively low-grade finished product.

The possibility of improving the grade of the material prior to calcination was given some consideration, though it was fully realized that deposits of this type would not easily be amenable to concentration by ordinary gravity ore-dressing methods. In fact, the removal of silica by such methods from any run-of-mine ore from even the higher grade alunites of the Utah lode-formations is regarded by U.S. Bureau of Mines investigators [55] as being impracticable.

Working on Chinese alunites, Hohorst and Wen [56] succeeded in reducing the SiO_2 content from 41.6% to 25.4% by simply crushing the material and removing all particles greater than 0.075 mm. This method, apparently taking advantage of the ready grindability of alunite compared with that of quartz, results in a slight concentration of iron as well as of alunite, and is obviously not applicable to deposits of the type found at Lake Campion.

Ishikawa [57] claims to have floated alunite from a siliceous gangue using as reagents 0.1 to 0.2% acetic acid or acetate and 0.1% of palm oil.

Some flotation work was accordingly undertaken on Campion alunite by another investigator but the results obtained were not sufficiently encouraging to warrant further work in this field.

Neither was the material amenable to gravity concentration or hydraulic classification, and so, except perhaps for a preliminary washing to remove water soluble salts, no suitable method was found for improving the grade of the ore prior to calcination.

The advantages which would follow the removal of the water soluble salts before thermal treatment of the ore appeared so great that considerable time was spent in attempting to find a satisfactory means of achieving this end. That none was found was due mainly to the poor settling and filtering properties of the material. A redeeming feature of this failure lies, however, in the possibility of being able to produce a marketable sodium and/or magnesium salt from the sulphates formed from these original water soluble salts during calcination. One hundred tons of the ore yields approximately 10 tons of K_2SO_4 and, if not washed before treatment, a further 5 tons of sodium and magnesium sulphates will also be recovered.

The separation of these salts from the potassium sulphate presents a major problem.

After the early test work, therefore, it was decided to concentrate on the production of a low grade fertilizer from unwashed ore rather than to aim at a final potash salt of high purity, unless this latter could be achieved by some subsequent crystallization cycle as opposed to removal of the sodium and magnesium salts by preliminary washing.

The simplest method seemed to lie in the recovery by crystallization from the leach liquors of glaserite, the double sodium potassium sulphate $K_3Na(SO_4)_2$ containing about 78% K_2SO_4 .

IV. PRE-CALCINATION PROCESSES

1. FILTRATION OF RAW ALUNITE:

Attempts were made to wash the water-soluble salts from the alunite by pulping with water and filtration of the resulting slurry. This work may be divided into three main sections, comprising filtration tests

- (i) without addition of possible filter aids;
- (ii) after addition of possible filter aids;
- (iii) after preliminary dehydration of the alunite.

A. Equipment Used.

Three different filter leaves were used for the vacuum filtration tests described in this section.

In the early work, a leaf 12 inches square was used (leaf A), giving a filtering area of 2 square feet. The filter medium was 10 ounce duck over coconut matting, and the filtrate was drawn away through holes in the piping constituting the frame of the leaf.

The large quantity of pulp required when using this leaf, together with the difficulty experienced in preparing homogeneous pulps from the moist ore, led to its use being abandoned in favour of a smaller leaf. This leaf (leaf B) was made in the same manner as the first, but was only 6 inches square with a total effective filtering area of 0.5 sq. ft. Tests made on the same pulp and under identical conditions, using both these filters, gave results in satisfactory agreement.

In making tests with either of the above leaves, the filter was immersed vertically for a measured period in a pulp tank at the bottom of which low pressure air could be admitted for agitation purposes if necessary. The cake was flood-washed by immersion in a water tank, and then allowed to drain under vacuum for the required period.

The leaf in each case was connected to a dry vacuum pump through a filtrate receiver. Filtrate was removed from the receiver by a centrifugal pump set below the outlet of that vessel, while a moisture trap was included between the receiver and the dry vacuum pump to prevent liquid passing over into this pump. Pumps of the latter type are designed with small clearance and would be injured by liquid, hence the need for the above precaution.

Leaf C was used for all later tests. It consisted of a small disc over the under surface of which the filtering medium was stretched, while from the centre of the upper surface a tube could be led to the vacuum equipment. Thus in making a test, the leaf could be immersed in a pulp, vacuum applied and the filtrate drawn through the filtering medium (held away from the upper surface by radial ridges within the disc) into the body of the disc and then away to the filtrate receiver. The effective filtering area was 0.1 sq. ft.

In making filter leaf tests, the operation of a continuous vacuum filter was always kept in mind. While under vacuum, the test leaf was submerged for the chosen cake formation period, then immersed in the washing tank, and finally removed and held with the drain pipe down for the draining and drying time allotted.

When using leaf C, the operator had the choice of four different filtering media. These were respectively calico, and 10, 15 and 17½ oz. duck, the weights representing the weight of the dry cloth per square yard.

To determine which of these media was most suitable for handling the raw alunite, filtration tests were carried out on a 2 to 1 pulp made up from an air dried sample of the ore. The vacuum was 26 inches and a three minute filtration cycle was observed. The results are shown below in Table 3.

Table 3. Filtration of Raw Alunite using Different Filter Cloths:

Filter Test No.	Filter Cloth	F i l t e r C a k e			
		Wet gm	Moisture %	Dry Cake	
				gm.	gm/sq.ft.
1	Calico	21.2	31.0	14.6	146
2	10 oz.	25.8	31.8	17.6	176
3	15 oz.	24.0	30.4	16.7	167
4	17½ oz.	23.0	29.6	16.2	162

With the clarity of the filtrate much the same in each test, it is apparent that the 10 oz. duck is the most suitable for this work of the four cloths tested. It was accordingly used in all subsequent filtration tests on raw alunite pulps.

B. Experimental Details:

- (i) Filtration without addition of possible filter aids:

These tests were carried out using leaf A described above.

The conditions of the tests were such as to duplicate as closely as possible the operating conditions of a rotary drum filter of the Oliver type, running at 40% submergence and 6 minute and 3 minute cycles, respectively. The pulp ratio was varied between 2 water : 1 solids and 2.3 water : 1 solids, giving pulps of specific gravity between 1.3 and 1.25. The material was obtained as a homogeneous pulp only after 30 minutes treatment in a mechanical agitator. The pulp so obtained showed no tendency to settle even after 24 hours standing.

The thickness, wet weight per square foot, and moisture content of the filter cake were determined, after which the water-soluble salt content of a sample of the dry cake was estimated.

The conditions and results of some of these tests are shown in Table 4.

The cakes formed were approximately 0.1 inch in thickness, which is on, if not below, the lower limit for practical handling. It was found possible during the tests, however, to blow the cake cleanly away from the filter cloth with small air pressures of the order of 5 lb./sq. in.

From the results it is evident that -

- (a) To treat 350 tons per day, the filtering area required would be between 3820 and 4080 sq. ft. for the usual

Table 4. Filtration of Raw Alunite - no filter aids.

Filter Test No.	Filtration Conditions					F i l t e r c a k e				
	Cake forming sec.	Washing sec.	Drying sec.	Equivalent Commercial Cycle min.	Ratio Water to Alunite	Moisture content of wet cake %	Dry cake lb./sq. ft.	Filter area per ton per 24 hrs. sq. ft.	Residual water-soluble salts in dry cake %	Washing Efficiency % *
5	144	80	60	6	2	33.0	0.59	15.8	0.89	81.8
6	72	40	30	3	2.3	33.1	0.40	11.7	1.02	79.1
7	72	40	30	3	2.3	36.1	0.43	10.9	0.98	79.9
8	72	-	72	3	2.3	31.7	0.43	10.9	1.32	73.0

* The unwashed alunite contains 4.88 per cent of water-soluble salts.

3-minute filtration cycle. Taking into consideration the inevitable fluctuations of plant conditions and the deterioration of the filter cloth due to such factors as cover-blinding, these figures would be in the vicinity of 5600 sq. ft. This filtering area is equivalent to seven filters 14 ft. diameter x 18 ft. long, or five 14 ft. x 24 ft. machines.

(b) Even if it proved practicable to reduce the cycle time to, say, $1\frac{1}{2}$ minutes, a very large area (approx. 3600 sq. ft., see Filter Tests 60 and 61) would still be required and the thickness of the cake would probably in itself prove prohibitively small.

(c) The cake is very impervious and carries an uncommonly large water content. These two factors result in an unsatisfactory washing efficiency.

(d) Less dense pulps, though giving a higher salt removal efficiency, would require still larger filter areas to handle a given tonnage.

(e) The above factors, together with the high water consumption involved, combine to make impracticable the removal of the soluble salts from untreated alunite by pulping with water, followed by filtration and washing.

(ii) Filtration after addition of possible filter aids:

Attempts were made to improve the filtration conditions by the addition of certain filter aids to the pulp.

Owing to the difficulty of obtaining suitable quantities of homogeneous pulps, it was found expedient to use filter leaf B throughout most of the following tests.

Before commencing a test, all pulps were conditioned in a mechanical agitator for 15 minutes in the presence of the required quantity of filter aid. The gelatin, filter alum and starch were added as solutions, while the lime was added

slowly as a powder containing 70% free CaO.

The calcined alunite added in Filter Tests 14 and 15 was a -10+20 mesh product which had been calcined at a maximum temperature of 750°C. and then washed free of water soluble salts. The results obtained using up to 10% of this material in the pulp were so poor that the tests were repeated using a more finely ground calcine. The minus 40 mesh fraction of the calcine resulting from a 750°C. roast of an unclassified material (see later, Calcination Test 25) was accordingly extracted with water, the fines classified off and the remaining granular portion used for admixture with the raw alunite. In pulps carrying even 20% of this calcine, the filter cakes formed were still very sticky and impervious and the general results were discouraging.

These tests were carried out under the following constant conditions:-

Filtration Cycle	3 minutes.
Filtering Medium	10 oz. duck
Vacuum	26 inches
Filter leaf used	Leaf B (Tests 7, 9-15, 20-25) Leaf C (Tests 16-19)

and the results are tabulated in Table 5.

Table 5. Filtration of Raw Alunite - filter aids added.

Filter Test No.	Reagent added		Ratio water to alunite	Filter cake		
	Nature	Quantity lb./ton		Moisture content %	Dry weight per sq.ft. lb.	W/S Salts in dry cake %
7		-	2.3	36.1	0.43	0.98
9	Gelatin	1	2	35.0	0.43	0.82
10	Filter alum	1	2.25	37.7	0.44	1.10
11	"	5	"	37.7	0.42	0.90
12	Starch	1	"	39.4	0.48	1.34
13	"	4	"	39.6	0.46	1.22
14	Calcined Alunite (coarse)	112	"	36.4	0.46	1.18
15	"	224	"	35.4	0.47	1.34
16	Calcined Alunite (fine)	0	3	29.9	0.25	n.d.
17	"	112	"	30.1	0.25	"
18	"	224	"	35.2	0.31	"
19	"	448	"	34.6	0.40	"
20	CaO	15	2.35	45.0	0.51	1.45
21	"	25	"	48.1	0.57	1.92
22	"	35	"	47.9	0.59	1.95
23	"	45	"	48.7	0.61	1.99
24	"	55	"	55.5	0.86	2.83
25	"	45	5	47.0	0.40	1.11

From the table it will be seen that the addition of gelatin, filter alum and starch gave filter cakes only insignificantly greater than those obtained without any additions to the pulp, while the moisture content of the cakes showed slight increase.

After allowing for that portion of the cake made up of the added calcine, it is evident that the addition of leached calcine to the raw alunite will not provide the solution to the problems associated with the filtration of that material.

The only effective way to build up reasonable cakes seems to lie in the neutralization of the acidity of the ore and the consequent flocculation of the particles. The results of Test 24 show that it is possible to reduce the number of filters required by half by using 55 lb. of lime per ton of raw alunite. On the other hand, a very moist cake is discharged under these conditions and the residual water-soluble salt content of the dried cake is 2.83%. The sharp rise in the weight, per square foot, of cake obtained between CaO additions of 45 and 55 lb. per ton indicates that, at the lower lime additions, the CaO is consumed in neutralizing the acidity of the ore, while at about 45 lb. per ton the lime is sufficient, in addition, to precipitate as hydrate all the water-soluble magnesium associated with the alunite. Beyond this stage, the alkalinity of the pulp rises rapidly with consequent improvement in filtration properties. The quantities required are, however, so large as to preclude the use of lime as a filter aid in commercial practice. Moreover, the treatment has very little effect other than a replacement of the soluble sodium salts of the alunite by calcium salts, which salts would doubtless be just as troublesome in subsequent treatment stages as those already present.

A further series of tests were made in which increasing quantities of various reagents were added to the pulp prior to filtration. Filter leaf C was used throughout these tests, which were carried out under more rigidly controlled conditions than were possible when operating with the alternative equipment used in the work already described.

Though the filtration conditions varied slightly from one set of tests to another, all tests with any one reagent were carried out under strictly comparable conditions, and with a blank test for purposes of comparison. Thus the pulp ratio may have varied slightly from one set to another, but was constant and known for any one set. The same applies to such factors as temperature and vacuum.

The following lists the limits of such variations:-

Pulp ratio	1.9 to 2.1 water to 1 solids.
Temperature	15°C. to 21°C.
Vacuum	25½ to 26½ inches.

The constant factors were as follows:-

Filter medium	10 oz. duck
Filter area	0.1 sq. ft.
Conditioning time	3 minutes.
Cake forming	72 seconds
" draining	34 seconds
" washing	
(flood wash)	40 seconds
Cake drying	34 seconds.

The results of these tests are set out in the following table (Table 6).

Table 6. Filtration of Raw Alunite - filter aids added.

Filter Test No.	Reagent added lb./ton	F i l t e r C a k e		
		Moisture Content %	Dry weight per square foot lb.	W/S salts in dry cake %
NaOH:-				
26	0	28.3	0.32	0.53
27	3	29.6	0.35	0.55
28	6	29.0	0.36	0.66
29	10	30.6	0.43	0.81
30	20	32.6	0.51	1.13
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$:-				
31	0	27.3	0.34	-
32	$\frac{1}{2}$	28.2	0.34	-
33	$1\frac{1}{2}$	28.4	0.34	-
34	3	28.0	0.34	-
35	6	27.9	0.34	-
$Na_2HPO_4 \cdot 12H_2O$:-				
36	0	28.7	0.33	-
37	1	29.1	0.32	-
38	3	32.8	0.30	-
39	5	30.2	0.30	-
40	10	30.4	0.32	-
$MgCO_3$:-				
41	0	27.8	0.35	-
42	$2\frac{1}{2}$	29.6	0.33	-
43	5	29.6	0.34	-
44	15	29.7	0.33	-
Tannin:-				
45	0	28.7	0.34	-
46	$\frac{1}{2}$	29.9	0.30	-
47	$1\frac{1}{2}$	28.8	0.31	-
48	3	29.5	0.30	-
49	6	28.0	0.30	-
Starch:-				
50	0	29.4	0.31	-
51	1	28.3	0.29	-
52	3	29.5	0.30	-
53	5	29.0	0.30	-
54	7	30.4	0.28	-
Charcoal:-				
55	0	28.9	0.33	-
56	224	30.0	0.37	-

Of the reagents tried, caustic soda alone gave any increase in filtration rate and it is most probable that its use as a filter aid would not prove economically sound. The same would apply in the case of potassium hydroxide.

(iii) Filtration after Preliminary Dehydration of the Alunite:

There are a number of references in the literature to the improvement in settling and filtering rates of clays and like materials resulting from a preliminary dehydration at temperatures below 300°C.

Cook [58] for example, describes the handling of a clayey gold ore in Nevada with thickening and filtering properties in the raw state remarkably similar to those of the Lake Campion ore. On dehydration at a temperature greater than 110°C. the physical properties of the ore changed entirely, giving a product that settled and filtered almost as well as a quartz ore. The process, which also removed the sticky milling properties, was carried out in an ordinary commercial dryer at the cost of 100 lb. coal per ton of ore.

It was thought probable, therefore, that the filtering properties of alunite would be improved by subjecting the material to a preliminary low temperature heat treatment.

Five representative samples of a minus $\frac{1}{8}$ inch mesh product were heated for two hours at 110°C., 160°C., 210°C., 310°C., and 410°C., respectively. A sixth sample was thoroughly air dried at room temperature. The moisture content of this air dried sample was 5%, while the losses in weight of the original samples due to treatment at higher temperatures were 5.0% (110°C.), 5.8% (160°C.), 6.4% (210°C.), 7.4% (310°C.) and 15.6% (410°C.).

In pulping these products, the addition of water gave a rapid breaking down of the lumps to form a reasonably uniform slurry in the cases of the products dried at room temperature, 110°C. and 160°C. Heating to 210°C. gave a mass less readily broken down in water, and appreciably stickier than that obtained after heating at the lower temperatures, while the material treated at 310°C., though perhaps less sticky, was still more difficult to break down to a consistent slurry. Heating at 410°C. gave a hard lumpy material requiring mechanical grinding to obtain an even suspension.

Filtration tests were made on the air dried material, and that dried at 110°C. and 210°C. The following conditions were observed in all tests:-

Pulp ratio	2 water to 1 dried solids
Filtration temperature	15°C.
Filter medium	10 oz. duck
Filter area	0.1 sq. ft.
Vacuum	25 inches
Cake forming	72 seconds
" draining	34 "
" washing	40 "
" drying	34 "

The results are detailed in the following table (Table 7):

Table 7. Filtration of Dehydrated Alunite.

Filter Test No.	Temperature of Drying	F i l t e r c a k e		
		Thickness inch	Moisture content %	Dry Weight per sq. ft. lb
57	air	1/16-	29.3	0.26
58	110°C.	1/16-	30.2	0.27
59	210°C.	1/16-	33.6	0.21

From the results it appears that a decrease in filter area of something less than 5% only would result from drying the ore at 110°C., while dehydration at higher temperature would only add to the filtering difficulties.

The above 5% improvement would in practice be increased by a factor depending on the temperature rise of the pulp due to the pulping of material at a temperature approaching 110°C.

2. WASHING OF RAW ALUNITE BY COUNTER-CURRENT DECANTATION:

The feasibility of using counter-current decantation methods for washing the water soluble content from an ore or mill product depends to a large extent on the settling properties of the material.

In practice, the most valuable guide is the settling area required to handle one ton of solids per 24 hours by this method. This figure depends on the free settling properties of the solids and, taken in conjunction with figures showing the behaviour of the material under conditions of compression settlement, gives the number and dimensions of thickening tanks required to handle a given daily tonnage.

A general formula, suitable for application to experimental results, is derived as follows:-

Let A sq. ft. be required per ton of solids per 24 hours.
R ft. per hour be the rate of settlement at a given dilution.
T tons of water be separated per ton of solids per 24 hr. for a given dilution.
F tons be the weight of water to 1 ton of solids at a given dilution.
D tons be the weight of water to 1 ton of solids in the final discharge.

$$\begin{aligned} \text{Then } T &= \frac{62.5 \times 24 \times A \times R}{2240} \\ &= F - D \end{aligned}$$

therefore

$$A = \frac{1.493 (F - D)}{R}$$

General Settling Properties of Alunite:

Settlement tests on alunite taken direct from the deposit, carrying 18.6% moisture, and on the air dried material containing in this case 3.8% moisture, showed a remarkable difference in the settling properties of the two materials.

Whereas the settlement rate of the undried product, even at 10 to 1 dilution, is extremely slow, that of the air dried material is more satisfactory, though still slow. In addition, after 72 hours settling, the pulp ratio in the first case was 3.13 of water to 1 of solids, while in the second case the final ratio was 1.33 to 1.

The "dry" material formed a homogeneous slurry with water much more readily than the ore carrying 18.6% water. The behaviour of the drier material was checked on a second sample and the figures obtained were substantially the same as those in the first test.

The possible effect of ageing on the settling properties was determined by repeating general settlement tests after the pulp had been left standing for 4 days. Only very slight alteration in settlement rate or final density was noted.

The general behaviour of the two products during 72 hours settling from a 10 to 1 pulp is shown in the accompanying graph (Figure 1).

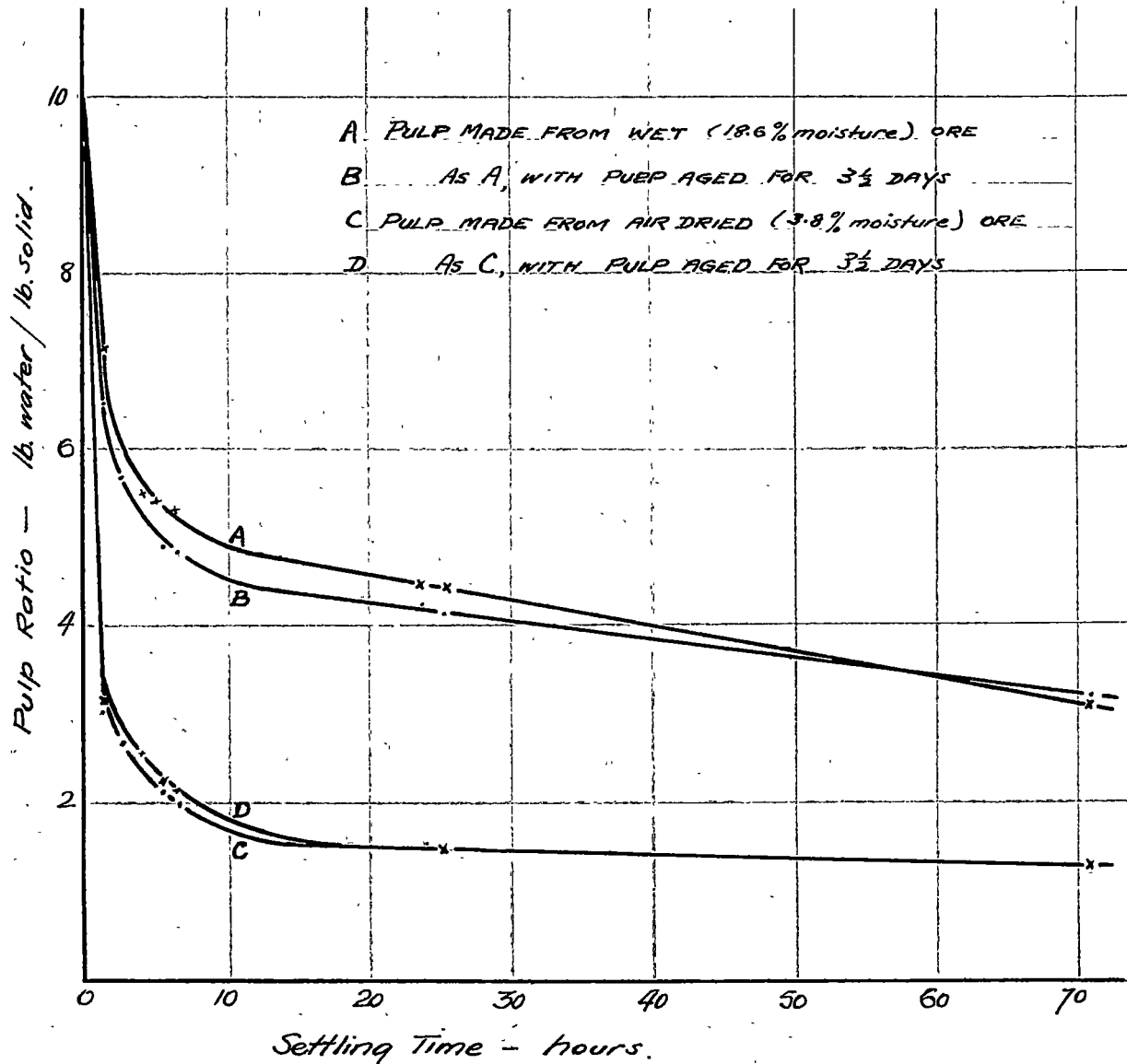


FIGURE 1. SETTLING CHARACTERISTICS OF RAW ALUNITE.

Efficiency of a System of Counter-current Thickeners:

The efficiency of any system of counter-current thickeners depends primarily on

- (a) the number of thickeners used,
- (b) the quantity of water used,
- (c) the pulp ratio of the thickener underflow.

A system of n thickeners is shown diagrammatically as follows:-

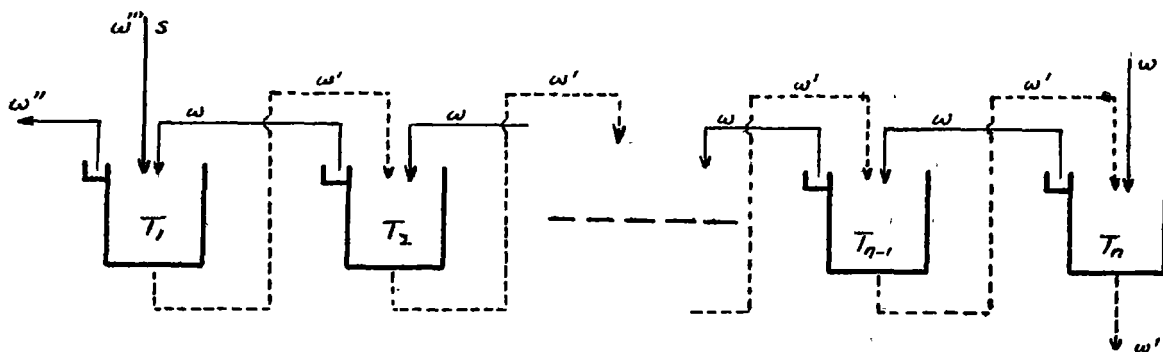


FIGURE II. COUNTER CURRENT WASHING SYSTEM.

Let $T_1, T_2 \dots T_n$ represent the tons of salts per ton of water in thickeners Nos. 1, 2 n respectively.

w = tons of wash water entering thickener n per day.

w' = tons of water leaving the system per day in the underflow from thickener n.

w'' = tons of water per day in overflow from thickener No. 1.

w''' = tons of water added per day to thickener No. 1 as moisture in the feed ($= w' + w'' - w$).

s = tons of salts added per day to thickener No. 1 as water-soluble salts in the feed.

Then equating the tons of salts into and out of each thickener per 24 hours we get the following set of equations:-

$$s + wT_2 = w'T_1 + w''T_1 = (w' + w'')T_1$$

$$w'T_1 + wT_3 = wT_2 + w'T_2 = (w + w')T_2$$

$$w'T_{n-2} + wT_n = wT_{n-1} + w'T_{n-1} = (w + w')T_{n-1}$$

$$w'T_{n-1} = wT_n + w'T_n = (w + w')T_n$$

The value of w can be controlled at will by the operator, while w' depends on the degree of compression settlement obtainable with a given ore. s and w''' are characteristics of the ore being handled, with w'' directly dependent on the values of w , w' and w''' .

Thus, with w' , w''' and s obtained experimentally the above equations can be solved for $T_1, T_2 \dots T_n$. That is, the extent to which the removal of water-soluble salts has proceeded at any given stage in a multi-stage system can be determined, or, alternatively, the efficiency of a system containing a given number of units. Or it may be that the number of thickeners required to reduce the water-soluble salt content to a given figure is sought.

The assumption that 350 tons of air dried ore would be treated per 24 hours to give the required daily yield of K_2SO_4 , leaves an adequate safety margin for calculating filtering and settling areas. This figure has been used in the previous work on filtration, and will be used throughout the following work on thickening of raw alunite.

The quantity of fresh water to be added daily can be arbitrarily chosen, say 875 tons (a ratio of water to solids of 5 to 2), while the moisture content of a sun dried sample of alunite was found to be 3.8%, giving 13 tons of water added with the feed. The water soluble salts in the same sample were 4.88%, giving a daily addition to the system of about 17 tons of these salts. Tests have shown that this material will settle in a reasonable time to a maximum pulp density of 1.33 water to 1 of solids, and so 467 tons of water will be discharged daily with the 350 tons of solids as the underflow from the last unit.

Thus, applying the above general equations to a series of four thickeners used to wash raw sun dried alunite, we obtain the following four simultaneous equations:-

$$\begin{aligned} 17 + 875 T_2 &= 421 T_1 + 467 T_1 = 888 T_1 \\ 467 T_1 + 875 T_3 &= 875 T_2 + 467 T_2 = 1342 T_2 \\ 467 T_2 + 875 T_4 &= 875 T_3 + 467 T_3 = 1342 T_3 \\ 467 T_3 &= 875 T_4 + 467 T_4 = 1342 T_4 \end{aligned}$$

Solving these equations, the values of the salt concentration in each thickener are given by -

$$\begin{aligned} T_1 &= 0.0370 \\ T_2 &= 0.0182 \\ T_3 &= 0.0081 \\ T_4 &= 0.0028 \end{aligned}$$

These figures show that the use of 4 counter-current washing thickeners would, under the above conditions, result in reducing the percentage of water soluble salts in the furnace feed from 4.88% in the unwashed ore to 0.37% if washing by this means were practised.

Similarly, it can be shown that about the same percentage of residual salts would be present if the amount of water used were increased by 25% and the number of thickeners used decreased by the same percentage, i.e. if 1094 tons of water were added per 24 hours to a 3 unit system.

Determination of Required Thickener Dimensions:

Practically all methods described in the literature for making these determinations are based on the original work of Coe and Clevenger [59].

The determination of the required settling area and thickener depth can be made from a study of the settling characteristics of the pulp.

The two factors with which we are concerned are the behaviour of the pulp in the free settling zone and its behaviour during compression, or hindered, settling.

The free settling phase is that in which the particles fall practically unhindered by each other and it is the rates of settlement of the particles at various stages in this phase that decide the settling area required to handle a given tonnage.

In a thickener, the pulp in settling passes through various zones between the dilution of feed and the dilution of discharge. Thus, with a feed of pulp ratio 10 : 1 and a discharge of 1 : 1, there will be intermediate zones of 9 : 1, 8 : 1 2 : 1. The depths of these zones will vary, as will the rates of settlement in the different zones. Consequently the zone displaying the slowest settling rate, relative to the amount of water separated in that zone, will be the one that limits the size of the thickener. This is so because all the pulp must pass through this slowest zone, no matter what the rates above or below it may be.

Compression settlement occurs when the solids have become thickened to such an extent that the particles rest on, and are partly supported by, one another. Water is eliminated at this stage by the pressure of the particles on each other and in so doing forms channels which enable the commencement of the compression settlement stage to be recognized readily during experimental tests in glass vessels.

After the pulp enters the compression zone, further elimination of the water depends upon the area and depth of the tank and upon the stirring action of the thickener rakes. Thus the extent of, and conditions within, this zone partially determine the depth of the tanks to be installed.

Tests were made to obtain the necessary figures to give the thickener dimensions required to handle 350 tons of alunite per day. These tests are described below.

(A) Free Settlement, (Determination of settling area)

Pulps were made up from the air dried and the undried products, and comparative free-settlement tests carried out in graduated glass cylinders under the following constant conditions -

Temperature	19 C.
Specific gravity of Dry Alunite	2.63
Dry weight of alunite in each cylinder	24 gr.
Volume occupied by Alunite	9 c.c.

Settlement levels were read at two minute intervals for each pulp dilution from 10 to 1 to the beginning of compression settlement. This ~~latter~~ stage was reached at about 4 to 1 for the air dried sample and at about 6 to 1 in the case of the undried material. (See Figure I).

The results obtained were used for the determination of the settling area required to handle raw alunite under the two different conditions of moisture content. These results are set out in Table 8.

Table 8. Free Settlement of Raw Alunite:

(a) Moisture in original ore 3.8%

F	R ft/hr.	D	F - D	1.493(F-D)	A. sq.ft/ton/24 hr. 1.493(F - D)/R
3	-	1.33	1.67	2.49	Compression settling 36.5 20.5 18.4 17.8 17.6 18.8
4	0.04	"	2.67	3.98	
5	0.15	"	3.67	5.48	
6	0.34	"	4.67	6.97	
7	0.46	"	5.67	8.46	
8	0.56	"	6.67	9.95	
9	0.65	"	7.67	11.44	
10	0.69	"	8.67	12.94	

(b) Moisture in original ore 18.6%

3	-	3.33	-	-	Compression settling
4	-	"	0.67	1.00	
5	-	"	1.67	2.49	
6	-	"	2.67	3.98	
7	0.04	"	3.67	5.48	137
8	0.05	"	4.67	6.97	139
9	0.09	"	5.67	8.46	94
10	0.09	"	6.67	9.95	111

The above figures show that the minimum allowable area for settlement is 36.5 sq.ft/ton/24 hr. for the "dry" material and 139 sq.ft/ton/24 hr. for the undried ore.

Adding 10% to each for plant emergencies, the figures become 40 and 153 sq.ft/ton/24 hr., respectively.

These figures compare favourably with areas required for thickening other slow settling materials such as bauxite residues after H₂SO₄ digestion and water-floated clay. In the case of clay, cases are known where over 200 sq. ft/ton/24 hr. have been required to thicken from F = 60 to a discharge carrying about 20% water. The tonnages to be handled were, however, relatively small.

Thus to handle 350 tons per day the respective settling areas required would be 14,000 sq. ft. and 53,500 sq. ft.

Washing by counter-current decantation would therefore involve, for example,

(i) on air dried material, 3 series of 4 thickeners, each approximately 77 ft. in diameter.

(ii) On undried ore, 6 series of 4 thickeners, each approximately 106 ft. in diameter.

(B) Hindered Settlement. (Determination of depth of compression zone)

The following figures apply only to the air dried material.

Compression settlement tests were carried out at 19°C. giving the following results. (Table 9)

Table 9. Hindered Settlement of Raw Alunite:

Reading of pulp line a c.c.	Volume of Water (a-9)c.c.	Dilution Gm.water: 1 Solids $\frac{a-9}{24}$	Time interval t hours	Corres- ponding average dilution d	d x t
93	84	3.50	-	-	-
87	78	3.25	0.25	3.38	0.84
82	73	3.04	0.25	3.15	0.79
80	71	2.96	0.25	3.00	0.75
77	68	2.83	0.25	2.90	0.73
75	66	2.75	0.25	2.79	0.70
73	64	2.67	0.25	2.71	0.68
72	63	2.63	0.50	2.65	1.32
68	59	2.46	0.75	2.55	1.91
66	57	2.38	0.50	2.42	1.21
64	55	2.29	0.50	2.34	1.17
61	52	2.17	1.00	2.23	2.23
58	49	2.04	1.00	2.11	2.11
45	36	1.50	17.00	1.77	30.09
44	35	1.46	2.00	1.48	2.96
43	34	1.42	2.50	1.44	3.60
41	32	1.33	42.50	1.38	58.60
TOTAL			69.75		109.69

Hence the average dilution in the compression zone

$$= \frac{109.69}{69.75} = 1.56$$

and average specific gravity of pulp in this zone

$$= \frac{1.56 + 1}{\frac{1.56 + 1}{2.63}} = 1.32$$

Also,

Final density - solids to 1 part solution ... 1.33
Hours retention necessary to reach this
density (say) ... 48 (see graph)
Sq.ft./ton of solids/24 hrs. ... 40
Capacity in lb. dry solids/sq.ft./hr ... 2.33

To hold these quantities/sq.ft./hr. for 48 hours will mean
storage for 48 x 2.33 = 112 lb. solids
= 287 lb. pulp.

Hence depth of compression zone is

$$\frac{287}{62.5 \times 1.32} = 3.48 \text{ feet.}$$

(C) Determination of Thickener Dimensions:

Assuming 3 series of counter-current washing thickeners,
the following figures are now available -

Solids to be handled per 24 hr. per
thickener - tons ... 117
Settling area required - sq.ft./ton/24 hr.. 40
Total area required for thickener - sq.ft.. 4670
Diameter of thickener - ft. ... 77
Assume slope of raking arms in thickener -
in./ft. ... 1 1/4
Maximum depth of arms - ft. ... 3.75
Assume 2/3 of this depth ineffective due to
solids building up under rakes; so
ineffective depth - ft. ... 2.50

Determination of Thickener Dimensions (Contd.):

Total depth of thickener - ft					
Ineffective	2.50
Compression zone	3.48
Feed well	2.00
Total					7.98
					=====

Hence, to reduce the water soluble salts in air dried raw alunite from 4.88% to approximately one-thirteenth of this figure by counter-current washing in thickeners, it would be necessary to install 3 series of 4 thickeners, each unit to be 77 feet in diameter by 8 feet deep.

Filtration of Thickener Underflow:

Further de-watering of the pulp would be necessary to give a product of the nature required for the furnace feed. This would involve filtration of the underflow from the last thickeners of the series. As no washing of the cake on the filter would be necessary, a filter with high diametral submergence, of the order of 40%, could be used.

Filtration tests were made to determine the filtering area required to handle the 817 tons of pulp discharged daily from the washing thickeners. This pulp has a consistency of 4 parts of water to 3 of solids and was duplicated in the laboratory by making up a slurry of the required density using a sample of the air dried ore.

The tests were made under the following constant conditions:-

Filtering medium	10 oz. duck
Filtering area of leaf	0.1 sq. ft.
Vacuum	26 inches
Pulp ratio	4 water to 3 solids
Temperature	19°C.

The results are shown in Table 10.

Table 10. Filtration of Thickener Underflow:

Filter Test No.	Filtration Cycle		Filter Cake		Filtering area required sq.ft.
	Cake forming sec.	Draining etc. sec.	Moisture %	Dry cake lb./sq.ft.	
60	72	108	30.3	0.46	3550
61	36	54	30.4	0.35	2330

The last column gives the filtering area required to handle the equivalent of 350 tons of ore per 24 hours under test conditions. It is usual to allow a generous margin in calculations of this kind to compensate for plant fluctuations, cloth blinding etc., and for pulps of the type under test it is reasonable to assume that the operating capacity of a filter is of the order of 0.7 times the test leaf capacity. So, applying this "cover-blinding factor" of 0.7 to the results of Filter Tests 60 and 61 above, we obtain filtering area requirements of 5070 sq. ft. and 3330 sq. ft. respectively, depending on the filtration cycle adopted.

Settlement of Dehydrated Alunite

If the settling rate of the unwashed alunite could be increased by a factor of at least two, removal of the water soluble salts by counter-current decantation would provide a reasonably cheap and efficient method for the commercial handling of this material. The figures obtained in the sections above, however, are such as to preclude the use of such a process for washing untreated or simply air dried ore.

In the hope that this ore would behave similarly to those described by Cook [58] and others, it was decided to carry out a series of settling tests on alunite partially dehydrated by heating to temperatures up to 400°C.

The samples described in Section IV, I, (iii) of this report were used for the test work. Pulp ratios of a consistency of 10 fluid to 1 solid were made up from ore which had been subjected to preliminary drying at room temperature, 110°C., 160°C., 210°C., 310°C. and 410°C. respectively.

The settling rates and pulp ratios of each slurry were recorded over a period of 28 hours, at first at 6 minutes intervals, but later at hourly or longer periods.

The pulp ratios are plotted against the time interval on the accompanying graph (Figure III.).

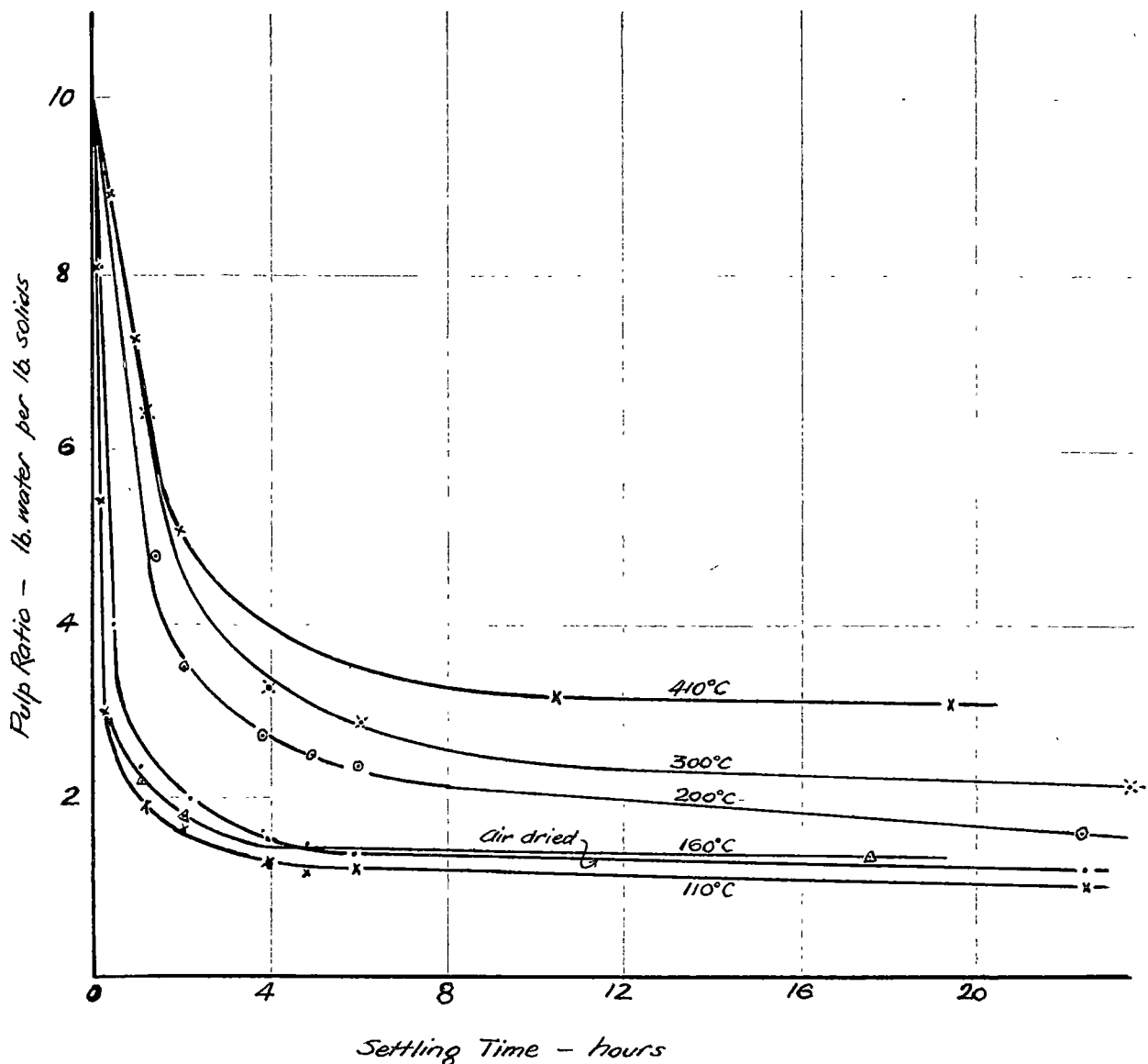


FIGURE III. SETTLING CHARACTERISTICS OF PARTIALLY DEHYDRATED ALUNITE.

From the results it is apparent that a slight improvement in the settling properties arises from a preliminary drying at 110°C., but preheating to temperatures above this figure causes a marked decrease in the rate of settlement.

The improvement due to the low temperature drying is, however, definitely insufficient to warrant such treatment in practice.

V. C A L C I N A T I O N

(1) PILOT PLANT:

The pilot plant consisted essentially of two units, a grinding unit and a calcination unit.

(i) The Grinding Unit:

This unit consisted of a horizontal cylinder made of 10-mesh screening for the earlier tests, later replaced by $\frac{1}{4}$ " screening. The cylinder, 18" long by 9" diameter, was closed at each end, with a feed hopper at one end. The air-dried material was fed in and forced against the screening by bricks rotating on a shaft along the long axis of the cylinder. It was brushed through the screen by wire brushes following the bricks.

With the cylinder made of 10 mesh screening, this crusher gave a product which was graded into three sizings in the following proportions:-

-10+20 mesh	20%
-20+40 mesh	40%
-40 mesh	40%

These grades were used as such in many of the early tests and were designated respectively coarse, middling and fine fractions.

With the 10 mesh screen replaced by the $\frac{1}{4}$ inch screening, a material containing only a small percentage of fines was obtained. In this case the grinder discharge was fed direct to the furnace without any preliminary grading.

(ii) The Calcination Unit:

The rotary kiln used in all calcination tests was 12 feet Long, made up of two 6 ft. sections; the external diameter was 25 $\frac{1}{2}$ inches, while the internal diameter, after lining with fire-brick, was 16 inches.

Four thermocouple holes were provided at 3 ft. centres along the furnace, each being fitted with chromel-alumel couples and terminals for millivoltmeter leads.

The cylinder revolved on rollers, commonly at the rate of 3 to 5 r.p.m., though the speed could be varied, if required, between 1 and 10 r.p.m.

The fall from the horizontal could be adjusted to a maximum of 1 ft. over the furnace length. The angle of inclination was adjusted by a hydraulic jack operating under a short length of channel iron welded to the furnace chassis.

All moving parts were driven by a $\frac{1}{2}$ h.p. motor, through a reduction gear coupled directly to the drive shaft by means of a flexible fibre coupling.

Variation of speed was obtained by providing different diameter pulleys which could be fitted at the reduction gear. The motor was situated under the cold end of the furnace cylinder and was enclosed in a light gauge iron cover to exclude dust and fine particles of material. A reversing switch was provided so that the furnace could be revolved in either direction.

At the feed end, the furnace was fitted with dust chamber, exhaust stack and hood and an automatic feeder capable of feeding quantities varying from 1 to over 500 lb. per hour.

At the discharge or combustion chamber end there was no gear to allow of the continuous removal of the calcined charge from the firebox, though such a fitting would have undoubtedly increased the ease of operation of the furnace.

The oil burner used was a Frank Saunders No. 1 non-rotary burner, capable of burning up to 6 gallons per hour and down to about 1 gallon per hour. The blower unit supplying air to the burner was mounted on insulating material on top of the combustion chamber.

The refractory for the furnace lining gave trouble during the earlier tests. An attempt was made to reduce heat losses by including a layer of diatomaceous earth between the furnace shell and the actual firebricks, but even during preliminary trials this arrangement proved mechanically unsuitable.

The furnace was accordingly relined with special $4\frac{1}{2}$ " thick firebricks, the insulating layer of diatomaceous earth being omitted. The bricks were manufactured from -

- (a) a highly bauxitic fireclay of good refractory properties,
- (b) a kaolinised andalusite schist with 35% andalusite and,
- (c) a fireclay grog, highly burnt and graded.

The quantities of these materials used were in the proportions of 6:2:1 by volume respectively.

After preliminary grinding, screening and pugging the mix was extruded, cut and repressed to standard size bricks, then dried and burnt at 1350°C . with 24 hours soaking.

This lining gave good service throughout the tests. Though the actual furnace operating time during the test work would not have been more than 250 hours, the furnace lining was subjected to fairly severe conditions due to the many heating and cooling stages passed through in the course of the nine month period over which the tests were carried out.

As originally lined, tumbling of the charge within the furnace was brought about by two straight longitudinal rows of tumbler bricks projecting some $2\frac{1}{2}$ " from the main lining surface. This resulted in the gases being given off in surges each half revolution and consequently in difficulty in controlling the roasting conditions. When relined, the two rows of tumbler bricks were so laid as to form a double helix along the length of the furnace. This arrangement resulted in better heating of the material and the continuous evolution of gas; and, in addition, allowed of a wider control of the time of through-put depending on the direction of rotation of the furnace.

(2) CALCINATION TESTS:

In all the following calcination work, the time of calcination refers to the period elapsed between commencement of the feed and the appearance of a steady flow of calcine at the discharge end. The temperature of calcination is given as the reading shown at the thermocouple nearest the discharge end and may be 25° to 50°C . below the maximum attained for the short period just prior to discharge from the kiln.

Coarse, middlings and fines refer respectively to the -10+20 mesh, -20+40 mesh and -40 mesh fractions into which the crusher discharge was graded. An ungraded feed is qualified as such by the sizing of its coarsest fraction.

Calcining the raw alunite at high temperatures (around 900°C.) for a prolonged period results in a loss of 33% in the original weight of the dry alunite, mainly as SO₃ and combined water. In calcination tests reported, the "additional ignition loss" refers to the weight lost when a sample of the calcine from a pilot plant roast is subjected to a further ignition in the laboratory muffle at temperatures between 900° and 950°C. for 1 to 2 hours. By this treatment, total thermal decomposition of the sample can be assumed.

The efficiency of a roast depended primarily on the percentage of the original K₂O content of the alunite which was rendered water-soluble by the calcination process. This figure was obtained by determining the total K₂O content of the calcine sample by fusion with sodium carbonate and estimating the percentage of K₂O in the melt. The water-soluble K₂O was determined by extracting 70 grams of the calcine with water under strictly standardized conditions and determining the K₂O in the extract by the cobaltinitrite method.

The potash alunite content of the material fed to the furnace throughout these tests averaged between 64% and 65%, while 21% was the average silica figure.

A. Furnace Characteristics

(i) Capacity:

Tests were undertaken to determine the maximum capacity of the kiln. A temperature of 800°C. and a calcination time of 15 minutes were chosen arbitrarily and carefully maintained during each test. The feed consisted of air-dried middlings.

At feed rates of 1 cwt. per hour and 2 cwt. per hour the efficiencies of calcination and of gas disposal were satisfactory, but when the feed was increased to 3 cwt. per hour there were obvious signs of choking within the kiln. The draught through the kiln was insufficient to carry the products of decomposition up the stack, and it was apparent that the working capacity of the kiln had been exceeded.

(ii) Fuel Consumption:

A check on the fuel consumption was made during the tests described in section (i) above, the results showing a three-fold increase in the quantity of oil consumed when the feed was increased from 1 cwt. per hour to 2 cwt. per hour.

The conditions and results of these tests are tabulated in Table 11.

Table 11. Rotary Kiln - capacity and fuel consumption.

Calcination Test No.	F e e d		Calcining Time min.	Fuel Consumption gal./hr.	Extra Ignition Loss %	K ₂ O Extraction %
	Material mesh	Rate cwt/hr.				
1	-20+40	1	15	0.55	8.5	72.4
2	"	2	"	1.70	9.1	69.9
3	"	3	"	Kiln capacity exceeded		

(iii) Time of Through-put:

Tests conducted at speeds of rotation of 3 and 5 revs. per min. and with the inclination of the kiln at $\frac{1}{2}^\circ$ and the direction of rotation opposed to that of the tumbling spirals showed that the maximum period for which material could be retained in the furnace was about 60 minutes.

By increasing the rate of rotation and the slope of the kiln, it was found that the minimum practical period of calcination was 5 minutes.

B. Calcination Variables

The main variables that could affect the efficiency of calcination are

- (i) Temperature of calcination
- (ii) Time of calcination
- (iii) Sizing of feed
- (iv) Rate of feed.

Work was carried out to determine the optimum calcination conditions by a series of tests in which three of the above factors were kept constant with the fourth varied between what were considered practical limits.

(i) Temperature of Calcination:

A number of pilot plant calcinations were undertaken at temperatures between 700°C. and 900°C.

The conditions and results of these tests are shown in Table 12.

Table 12. Calcination at Various Temperatures.

Constant conditions -
 Sizing of feed -10+20 mesh
 Rate of feed 1 cwt. per hour
 Time of calcination 20 minutes.

Calcn. Test No.	Calcn. Temp. $^\circ\text{C.}$	Extra Ignition Loss %	W/S salts in Calcine %	K ₂ O in Calcine		K ₂ O Extraction %
				Total %	Water-soluble %	
4	720	12.0	29.5	7.90	5.93	75.1
5	750	8.8	24.9	7.98	6.13	76.8
6	800	7.2	22.9	8.13	6.34	78.0
7	850	5.8	21.7	8.67	6.13	70.7
8	900	2.3	18.2	9.04	5.11	56.5

From the above figures it appears that at 850°C. the reaction has already commenced between the alunite and silica, giving rise to insoluble potassium alumino-silicates. Above 850°C. the extent of this reaction increases rapidly, with a resulting marked decrease in the percentage of water-soluble potash in the calcine.

The decided decrease in the total water-soluble salt content of the calcine with increasing temperatures of calcination is explained by the formation of potash alum at the lower temperatures, followed by decomposition of this soluble compound to form potassium sulphate and alumina at the intermediate temperatures.

At 900°C. there is probably some potassium aluminate formed in addition to the insoluble potash compounds resulting from a reaction between the alunite and the gangue material.

(ii) Time of Calcination:

A further series of tests was conducted to determine the effect on the potash recovery of varying the time of calcination at different temperatures.

When the periods of calcination were only of the order of 5 to 10 minutes, a fairly high rate of feed had of necessity to be maintained. This was advantageous in that some variation in the rate of feed between short and long period roasts would have the effect of keeping the actual loading conditions within the furnace more comparable from one test to another.

The furnace feed for these tests was in all cases the -10+20 mesh material.

The results are tabulated in Table 13.

Table 13. Calcination for varying periods.

Calcn. Test No.	Calcn. Temp. C.	Time of Calcn. min.	Extra Ignition Loss %	W/S Salts in Calcine %	K ₂ O in Calcine		K ₂ O Extraction %
					Total %	Water-soluble %	
9	695	60	14.3	26.1	8.63	5.21	60.4
10	750	20	8.8	24.9	7.98	6.13	76.8
11	750	45	6.2	23.0	8.75	6.96	79.5
12	750	60	7.1	25.3	8.45	6.76	80.0
13	750	90	5.9	20.2	8.96	6.46	72.1
14	800	8	9.8	25.9	8.39	6.13	73.0
15	800	20	6.4	23.7	8.72	6.74	77.4
16	800	30	4.0	21.5	9.67	6.57	67.9
17	900	5	4.3	19.2	8.92	5.31	59.6
18	900	20	2.3	18.2	9.04	5.11	56.5

For the production of potassium sulphate it is obvious that any temperature below about 720°C. is unsatisfactory unless, perhaps, a roasting time very much in excess of one hour be allowed.

The results of varying the calcination period of tests run at 750°C. indicate that no useful purpose is served by prolonging this period beyond an hour - optimum conditions seem to be attained after 45 to 60 minutes.

As material could be maintained in the furnace only for a maximum period of 60 minutes, Calcination Test 11 was run at a 45 minute rate and the resulting calcine sampled and, after cooling, fed again to the furnace to give the 90 minute thermal treatment of Calcination Test 13.

Tests 14-16 show that a period of 30 minutes in the kiln with a maximum temperature of 800°C. is excessive when using material of the nature fed during this series. In eight minutes, on the other hand, the degree of decomposition is insufficient to give a maximum recovery of potash, so that, when calcining at this temperature, some period intermediate between 10 and 30 minutes seems most satisfactory.

At 900°C. a temperature has been reached at which re-conversion of the potash from a soluble to an insoluble state has commenced even after as short a calcination period as 5 minutes.

(iii) Sizing of Furnace Feed:

The effect of the particle size of the feed on the efficiency of calcination was tested by two methods. In one, separate tests were run using first the -10+20 mesh material and then the -40 mesh product, while in the other, only one calcination was carried out on an ungraded minus 1 inch ore, from which the various sizing fractions of the calcine were separated and extracted independently.

It was not possible to obtain a reliable and detailed sizing analysis of, say, a minus 1 inch batch of raw alunite, owing mainly to the extent of the crumbling unavoidably associated with the process of screening. The calcine, however, could readily be graded, either by hand or in a mechanical grader.

The sizing of the calcine has therefore been taken as an indication of the sizing of the feed in the case of an unclassified feed. This is reasonable as the errors introduced are small, consisting as they do of losses of fines as flue dust and some slight crumbling of the bigger particles due to the tumbling action within the furnace. Usually a given nodule retains its shape and size quite well during its passage through the furnace.

Table 14 shows the conditions under which this series of tests was conducted, and the results of the calcination of alunite under such conditions.

Table 14. Calcination at Different Sizings.

Calcination Test No.	Calcination Temperature °C.	Time of Calcination min.	Furnace Feed			Extra ignition loss %	W/S Salts in Calcine %	K ₂ O Extraction %
			Rate lb/hr.	Fractions				
				Sizing	Per cent of feed			
19	750	60	56	-10+20	100	8.0	26.7	80.9
20	750	60	64	-40	100	7.6	24.5	67.5
21	800	17	112	-10+20	100	5.4	20.4	70.7
22	800	15	112	-20+40	100	8.5	25.3	72.4
23	900	5	168	-10+20	100	4.3	19.2	59.6
24	900	5	168	-40	100	2.0	13.7	36.3
25	750	60	88	-1" + 1/2"	2.0	11.9	25.0	58.7
				-1/2" + 1/4"	21.1	9.5	23.7	66.6
				-1/4" + 1/8"	27.5	8.2	25.4	78.2
				-1/8" + 1/40"	25.2	8.0	25.5	78.5
				-1/40" + 1/80"	18.9	8.1	28.4	78.5
				-1/80"	5.3	7.8	34.1	78.9
26	750	40	168	-1/4"	100	10.8	22.7	75.3

The figures for Tests 19-24 show that it would be bad practice to feed dry fines alone to a furnace of the type used for these pilot plant calcinations, even at low rates of feed similar to that adopted in Test 20. Apparently, a charge consisting of fines (minus 40 mesh) alone has the effect of impeding the flow of air through the kiln, and, indirectly, the ready removal from the body of the furnace of the gases of decomposition of the ore. In the case of high temperature roasts, an additional factor working against the use of fines is the existence of conditions more favourable to the reaction between the potash and the silica and/or alumina to form insoluble potassium salts.

From Test 25 it is apparent that decomposition of the alunite will not proceed to the desired stage if the nodule size is greater than $\frac{1}{4}$ inch, but below this size the potash recovery as K_2SO_4 from an unclassified feed is independent of the particle size, provided, of course, that too large a percentage of fines is avoided.

Test 26 was carried out to confirm the suitability of minus $\frac{1}{4}$ inch material, and also to accumulate calcine for subsequent leaching experiments.

(iv) Rate of Feed:

As stated previously (V, 2, A(i)), it was not possible to treat 3 cwt. per hour in the pilot plant kiln, while at 2 cwt. per hour the potash recovery was beginning to fall off. It appears, therefore, that the maximum desirable rate of feed would be about $1\frac{1}{2}$ cwt. per hour, with perhaps greater recovery efficiencies at rates between 50 and 150 lb. per hour. It was between these latter two rates, therefore, that calcinations were run when undertaken primarily to accumulate material for later test work.

The temperature gradient along the kiln during 750°C. roasts for 60 minutes at three different rates of feed are shown in Figure IV. (See C following).

The feed rates were 56, 88 and 105 lb. per hour and the recoveries of potash from the resulting calcines 80.9, 78.5 and 80.0 per cent, respectively. Thus within these limits the rate of feed does not appreciably affect the water-soluble K_2SO_4 content of the calcine.

(v) Summary of Sub-section 2B:

From the foregoing calcination tests it can be concluded that the best results are obtained from the material and equipment used throughout the work, when the main calcination variables are kept within the following limits:-

(a) Temperature of Calcination:- Maximum temperature of 750°C. to 800°C. As pointed out at the beginning of Sub-section 2, these temperatures are probably 25° to 50°C. below the true maximum temperatures attained in the furnace section between the end thermocouple and the furnace discharge. The temperatures at various points along the furnace are shown below in Figures IV and V.

(b) Time of Calcination:- Between 40 and 60 minutes for 750°C. roasts and between 15 and 20 minutes in the case of 800°C. tests. The time spent by the charge in the various temperature zones is also shown in Figures IV and V.

(c) Sizing of Feed:- Below one quarter inch and with a minimum of fines. A detailed grading analysis of a calcine resulting from a 750°C. roast on an ungraded minus $\frac{1}{4}$ inch feed is given in a later section dealing with the leaching of these calcines.

(d) Rate of Feed:- Between 50 and 150 lb. per hour.

C. Miscellaneous Tests

(i) Temperature Gradient in Furnace:

Though the temperature of the roast was controlled mainly from the reading at the thermocouple nearest the discharge end of the kiln, in the majority of tests readings were also taken periodically at the other three thermocouples. By this means some idea of the thermal conditions at various points in the kiln could be obtained. These latter readings served also as a guide to the steadiness of conditions within the furnace prior to and during the passage of ore through the kiln. Thus, when heating up the cold furnace, a steady reading of 750°C. might be obtained at No. 4 thermocouple (nearest discharge) an hour or so before the readings at, say, No. 2 were constant.

Figures IV and V below illustrate the temperature gradients for a number of typical roasts. Graphs A and C (Fig. IV) and C and D (Fig. V) show the effect on this gradient of different rates of feed during 750° and 800°C. calcinations.

Using the lower horizontal scale in Figure IV an idea is obtained of the time spent by the charge in the different temperature zones.

The corresponding scale in Figure V applies to all graphs except graph D where the time of calcination was 15 minutes as compared with 20 minutes for all the remaining tests.

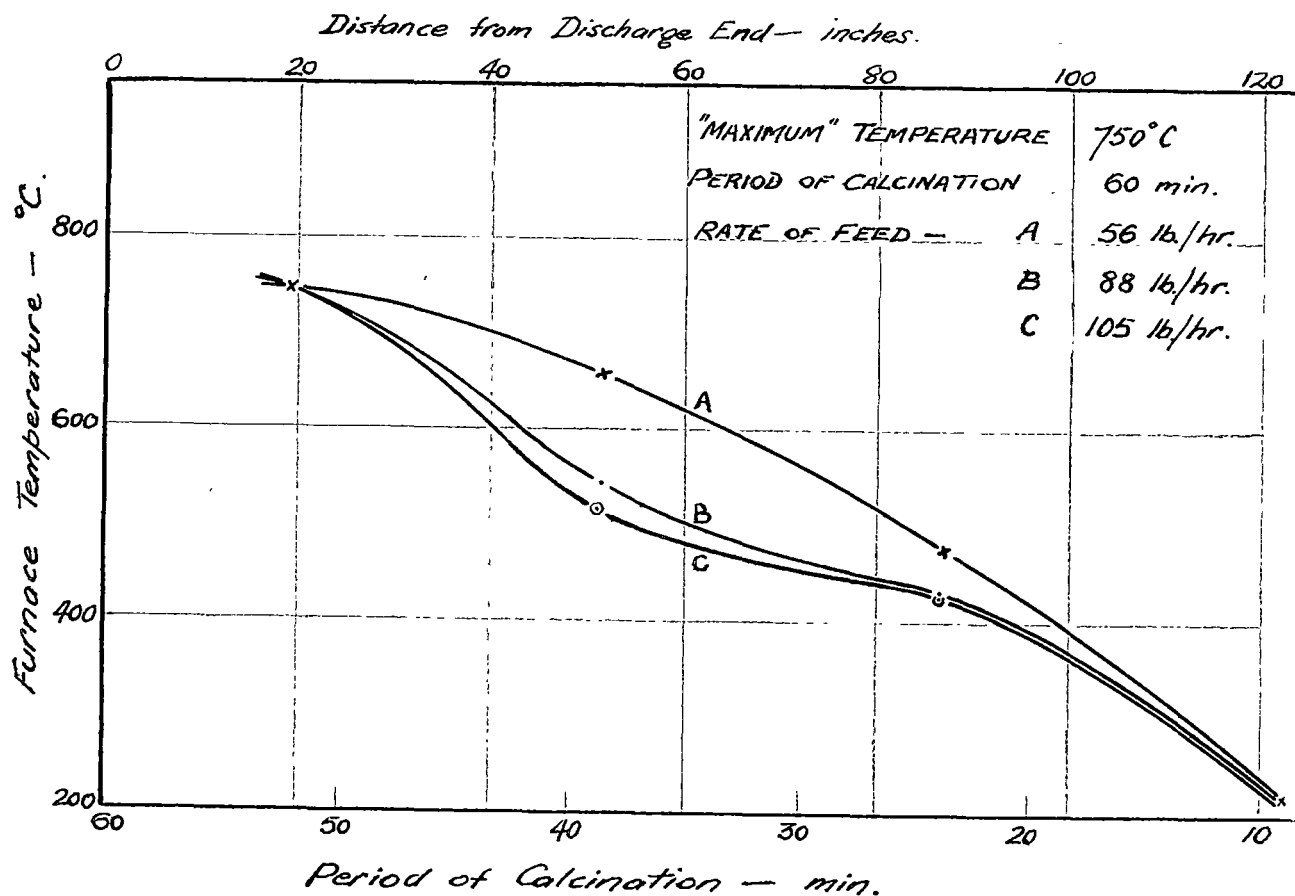


FIGURE IV. TEMPERATURE GRADIENT ALONG FURNACE.
(Varying rates of feed)

Using the figures for the extra ignition loss given in Table 12 and also those obtained for the loss of weight of the dry ore when heated at various temperatures between 110°C. and 410°C. (see IV.B iii), it is possible to draw a curve showing approximately the degree of completeness of decomposition at various temperatures.

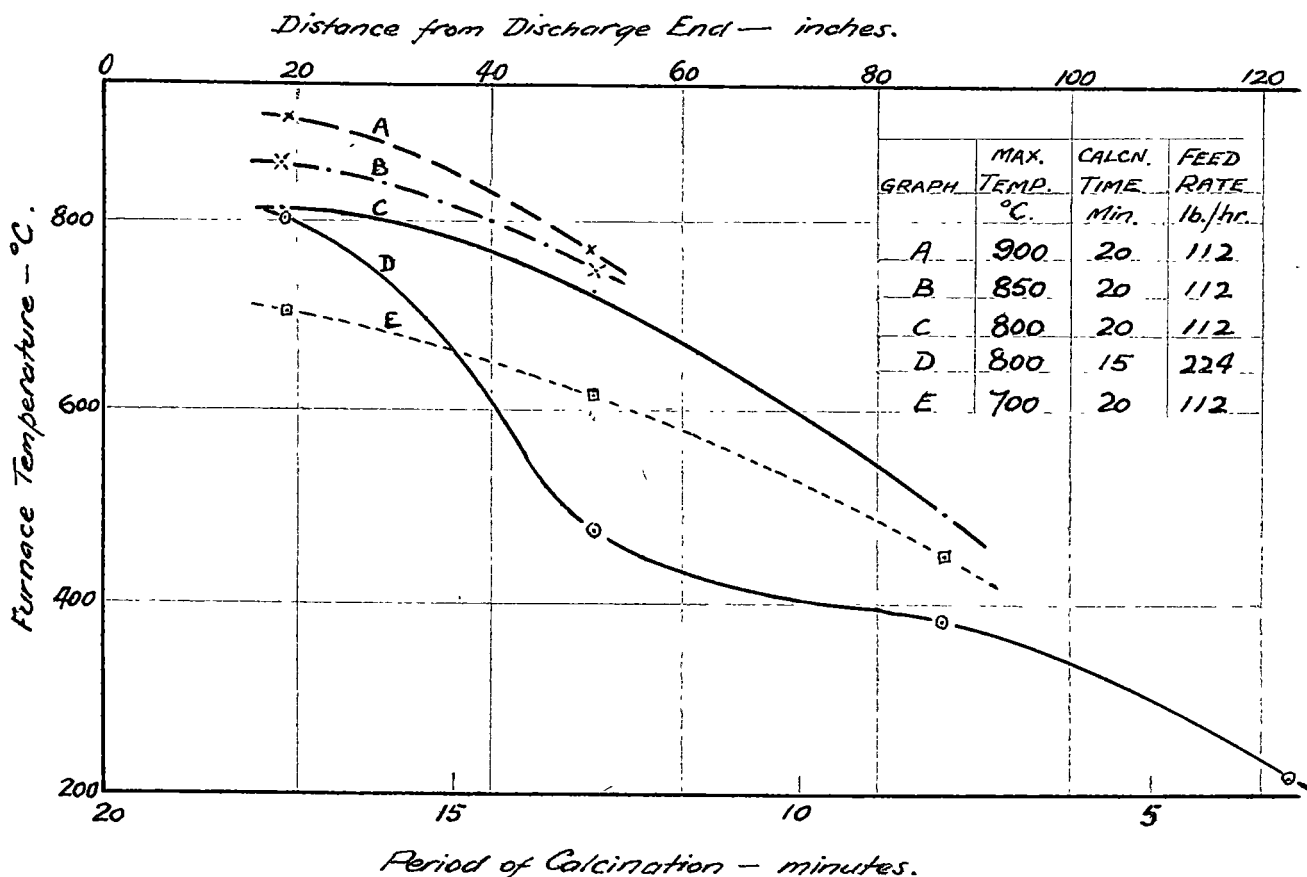


FIGURE V. TEMPERATURE GRADIENT ALONG FURNACE.
(Varying Maximum temperatures)

Experiments have shown that when thermal decomposition of the ore is complete, the resultant loss of weight is 33 per cent. For temperatures above 500°C. (obtained on pilot plant calcinations) the ordinate scale (P) of the graph referred to above is obtained from the relationship

$$P = \frac{33 - p}{0.33(100 - p)}$$

where p% = extra or additional ignition loss, as determined on the calcine after pilot plant roasting.

For temperatures below 500° (carried out on a laboratory scale in a muffle furnace) the corresponding values of P are obtained direct from weighings before and after calcination.

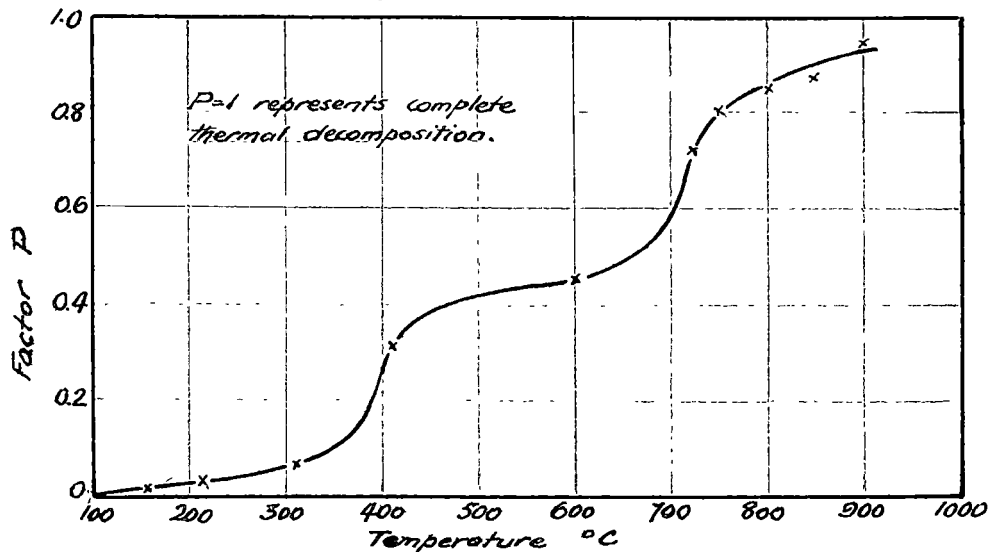


FIGURE VI. THERMAL DECOMPOSITION OF ALUNITE ORE.

Figure VI then, represents the curve obtained by plotting the values of P against the temperature of ignition and shows the two temperature regions in which decomposition is most active, viz. about 400°C. where loss of combined water takes place and between 700°C. and 800°C. where the evolution of SO₃ is most pronounced.

(ii) Effect of NaCl in Furnace Feed:

The fact that the maximum potash recovery from Lake Campion alunite by calcination and water extraction was only 80 per cent is due mainly, it is thought, to the production of insoluble potash salts at some stage of the calcination process. The thermal decomposition, in the presence of mainly siliceous gangue, of the mineral alunite itself would perhaps not be complete without either higher temperatures or longer periods of calcination than were found most suitable during the test work, and these latter conditions are those under which the formation of the insoluble potassium aluminates and silico-aluminates is favoured.

In determining the water-soluble potash content of a calcine, the leached residue was washed with an excess of water, thus ensuring the quantitative recovery of all available soluble potash salts.

It seemed possible, however, that the presence of sodium chloride in the ore fed to the furnace might in some degree have been responsible for this relatively low recovery. The glazing of common pottery by addition of salt to the kiln during the re-firing of the pottery is a well known process. Here the salt decrepitates, volatilizes and the vapours attack the surface of the clayware to give the typical salt glaze.

To test the possibility of a similar reaction taking place during the calcination of alunite contaminated with sodium chloride, three laboratory calcination tests were carried out on ore containing increasing amounts of NaCl. The tests were made at 750°C. on water-washed alunite (NaCl, trace only), unwashed alunite (NaCl 4.1%) and unwashed alunite to which an additional 5% NaCl had been added.

The calcines were leached under identical conditions, and the extracts assayed for potash.

The following percentages by weight of original dry unwashed ore were recovered as K₂SO₄:-

NaCl in feed - trace	8.72
NaCl in feed - 4.1%	8.58
NaCl in feed - 9.1%	8.47

The figures indicate that the presence of salt in the furnace feed may very slightly reduce the amount of potash recovered after roasting. This may be due to a glazing effect resulting in some of the otherwise water-soluble potash not being recoverable by water extraction.

The loss from this source is, however, negligible compared with the 20% loss from other causes.

It is interesting to note here that Blough and McIntosh [60] in an early patent suggest the mixing of NaCl with finely ground alunite prior to calcination at a temperature sufficiently low to prevent the formation of aluminates, and the subsequent recovery of sodium and potassium sulphates by leaching. HCl was recovered from the flue gases. Cross [61] claims satisfactory results from the roasting of a mixture of alunite and salt in the presence of steam at 500° to 700°C.

(iii) Behaviour of Chlorides during Calcination:

The water-soluble salts in the raw alunite consist largely of sodium chloride and it was considered likely that during roasting most of this chloride was converted to the sulphate.

The feed and calcine from Calcination Test 12 (see Table 13) were carefully sampled and the chlorine contents determined. The material used in Test 12 was -10+20 mesh, the maximum temperature 750°C., duration of roasting 60 minutes, and the K₂O recovery was 80%.

Analyses for chlorine of the feed and the discharge gave the following results:

Cl' in dry feed	2.49%
Cl' in dry calcine	0.018%
Loss of weight on roasting	30%
Elimination of Cl' on roasting ...	99.5% approx.

That this chlorine appears in the flue gases as hydrochloric acid is evident from the results of work described in (iv) below.

It does not concentrate in the flue dust under normal calcination conditions (see (vi) below).

(iv) Gas Analysis:

The main gases evolved during calcination of alunite ore from Lake Campion would be SO₂, HCl and water vapour. Though the temperature in the hotter zones would be sufficient to bring about the dissociation of SO₃ into SO₂ and oxygen, it was found that recombination had taken place almost completely by the time the gases reached the furnace flue. This could be due to a catalytic action of the dehydrated alunite in the cooler zones.

When calcining at maximum temperatures between 750°C. and 800°C. the temperature of the flue gases at the base of the stack was found to vary between 350°C. and 400°C.

The relative amounts of H₂SO₄ and HCl that could be obtained from this source would be an important factor in any subsequent process involving acid leaching of the potash residues for recovery of alumina.

A rough theoretical estimation may be made by considering the calcination at, say, 800°C. of 100 lb. of dry ore.

Thus 100 lb. ore contains 2.49 lb. Cl, 99.5% of which is lost on ignition (see (iii) above).

Therefore HCl available = $.995 \times 2.49 \times 1.028$ lb.
= 2.55 lb.

Also 100 lb. ore contains 64.6 lb. alunite, equivalent to 25 lb. SO₃ of which 75% is available by complete decomposition of the alunite to K₂O.3Al₂O₃.SO₃. The "extra ignition loss" when calcining at 800°C. averages 7%. Therefore decomposition can be regarded to be only 85% complete (see Fig. VI).

Hence, SO₃ available = $.85 \times .75 \times 25$ lb.
= 15.9 lb.
H₂SO₄ equivalent = 19.5 lb.
H₂SO₄/HCl = 7.65

During a pilot plant calcination test at $800^{\circ}\text{C}.$, a sample of flue gas was obtained by suction from the flue into an evacuated vessel, followed by absorption in caustic soda solution. On analysis, this sample showed an $\text{H}_2\text{SO}_4/\text{HCl}$ weight ratio of 8.0. The theoretical ratio would approach this figure more closely if consideration had been given to the small amounts of water-soluble sulphates present in the feed to the furnace.

Thus in treating 350 tons of unwashed ore per day, about 8.9 tons of HCl and 68 tons of H_2SO_4 could theoretically be recovered every 24 hours. These are the theoretical requirements of acid for the extraction of 4.1 tons and 23.6 tons of alumina, respectively.

The recovery of these acids in practice should present no insuperable difficulties, though such factors as dilution and moisture content might introduce complications.

It was found by other investigators that the HCl could be absorbed readily and selectively by passing the gases through water, while the SO_3 fog was recovered in acid towers containing concentrated H_2SO_4 .

(v) Dew Point of Flue Gases:

The gases evolved during calcination of this ore are very corrosive, and their corrosive action is, of course, increased many fold in the presence of moisture.

It is therefore necessary to have some idea of the dew point of the flue gases to assist the designing engineer in determining the dimensions and material of construction of the furnace stack.

The apparatus used in the determination of the dew point of the flue gases from the pilot plant is illustrated in Figure VII.

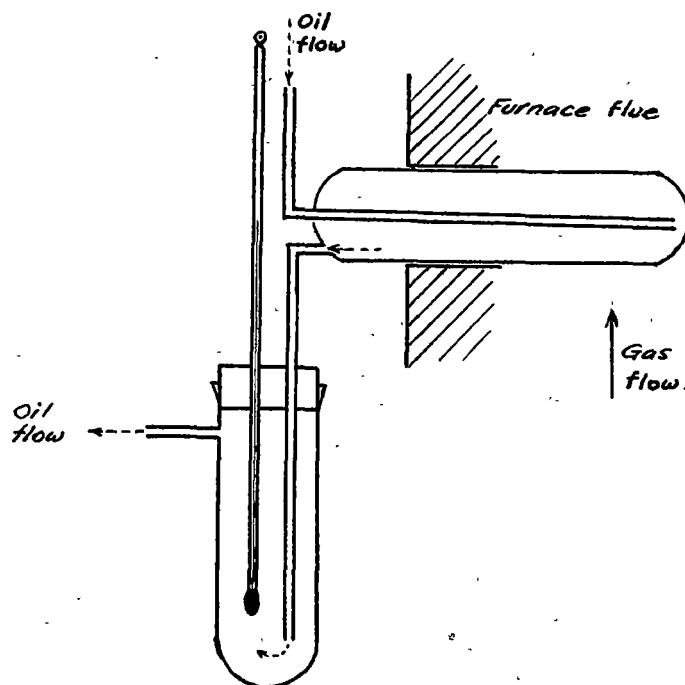


FIGURE VII. DEW POINT APPARATUS.

Hot cylinder oil was circulated by siphon flow from a two gallon storage vessel, heated on an electric hot plate and protected from air currents by screening. The glass tube carrying the thermometer and the connection between this tube and the dew point tube were insulated by binding with asbestos cloth and string.

To make a test, the oil flow was started and allowed to continue until constant temperature conditions existed throughout the apparatus. The glass surface of the dew point tube was cleaned and degreased in petrol, then carefully dried and polished. The tube was inserted into the path of the flue gases through a suitable opening in the flue, withdrawn and quickly examined for the presence of moisture. Several examinations were made for each temperature tried.

Tests were made at 140°C., 100°C., 90°C. and 70°C., respectively. No dew appeared at the higher of the two temperatures, but was in evidence at 90° and 70°C. It was therefore concluded that the dew point of the flue gases was about 90°C., a result subject to the limitations of the apparatus used and of the procedure adopted.

(vi) Flue Dust:

Before commencing Calcination Test 26 (see Table 14) the furnace was carefully cleaned by running for two hours with no feed or oil, but with the air tap fully open. All the dust accumulated in the flue dust chamber and that portion of the stack connected directly with the kiln was removed by thorough brushing.

During the progress of the test an appreciable amount of fines was air-classified at the feed entrance to the furnace. This material accumulated around the feed hopper and for the purposes of this rough approximation, was included in the total weight of flue dust collected. In practice, leakage of fines at this point would be minimized; but the fines collected here in the pilot plant test would appear as flue dust in full scale operations. Analyses were made, however, only of the dust collected from within the dust chamber.

The feed consisted of ungraded minus $\frac{1}{4}$ inch ore, the temperature was 750°C. and the time of calcination 40 minutes.

The results were as follows:-

Ore fed to furnace	672 lb.
Total flue dust collected	11.7 lb.
Flue dust as percentage of feed	1.7 per cent.

The flue dust collected from the dust chamber was sampled and extracted with excess of hot distilled water. The extract was analysed and the results are shown in Table 15.

Table 15. Analysis of Flue Dust.

Radical	Percent of Flue Dust	Percent of Water-soluble fraction
SO ₄	16.99	76.01
Cl	.36	1.61
K	.67	3.00
Al	1.66	7.43
Mg	.44	1.97
H	.03	0.13
Na (by diff.)	2.20	9.85
Insoluble	77.65	-
Combined as simplest salts.		
Al ₂ (SO ₄) ₃	10.51	47.0
MgSO ₄	2.20	9.8
K ₂ SO ₄	1.49	6.7
H ₂ SO ₄	1.47	6.6
Na ₂ SO ₄	6.06	27.1
NaCl	0.62	2.8
Total	22.35	100.0

The results verify the conclusion that the chloride in the unwashed alunite does not concentrate in the flue dust during calcination. With the possible exceptions of the free acid and sodium sulphate contents, the nature of the flue dust is similar to that of a calcine obtained from a low temperature roast, with potassium alum as the major soluble constituent.

D. Nature of Calcine:

(i) Physical Characteristics

The colour of the raw alunite varies between light and dark grey. This colour is retained at temperatures below about 400°C.; between 400°C. and 600°C. the calcine changes over to a dark pink colour, while as the temperature increases above 600°C. the intensity of the pink colouration falls off with increasing temperature until at 1000°C. the material is only faintly coloured.

As previously pointed out, the size and shape of the feed particles do not alter very extensively during the passage through the kiln. In structure, however, the calcined nodules are much less friable than those of the unroasted ore; the latter crumble readily at slight pressures, whereas the calcine lumps cannot be broken down at finger pressure. This structure is retained even after prolonged contact with water, a characteristic which is of great value when considering methods of leaching out the water-soluble constituents.

The structure remained unaltered when a sample of -10+20 mesh calcine was poured direct from the furnace (running at 750°C.) into cold water. After slow agitation for some minutes, the percentage of minus 120 mesh material formed was well below 1 per cent. Prolonged mechanical agitation of moderate violence would, of course, result in the production of large amounts of slimes.

A cubic foot of loosely packed average calcine weighs between 50 and 60 lb., giving an apparent density much the same as water. The specific gravity of a typical sample of water-leached calcine was found to be 2.86.

The angle of repose would be between 35 and 40° from the horizontal.

The average specific heat of a typical calcine sample was determined as 0.245 calories per gram over the temperature range 25°C. to 500°C.

The freshly calcined material is hygroscopic, even the minus $\frac{1}{4}$ inch calcine absorbing atmospheric moisture to the extent of two to three percent of its own weight.

(ii) Chemical Characteristics

A calcine produced under favourable conditions contains between 22 and 26 percent of water-soluble salts, consisting of sulphates of potassium, sodium, and aluminium derived from the alunite itself, and sulphates of sodium, magnesium and calcium arising from the saline water content of the raw ore. Iron and chloride are also present in varying small amounts.

The following analyses are typical of the water-soluble salt content of calcines obtained at 750°C. and 800°C., respectively.

Table 16. Analyses of Water-Soluble Content of Calcine

Water Soluble Salt	800°C. roast (20 minutes)		750°C. roast (60 minutes)	
	Percent of W/S Salts	Percent of Calcine	Percent of W/S Salts	Percent of Calcine
K ₂ SO ₄	54.70	12.96	49.90	12.62
Na ₂ SO ₄	27.64	6.55	29.59	7.48
MgSO ₄	10.48	2.48	10.30	2.61
Al ₂ (SO ₄) ₃	4.48	1.06	8.71	2.21
CaSO ₄	1.46	0.35	1.04	0.26
NaCl	1.09	0.26	0.46	0.12
Fe ₂ (SO ₄) ₃	0.15	0.04	Trace	Trace
Total	100.0	23.7	100.0	25.3

The analyses show that at the higher temperature the amount of soluble aluminium is substantially reduced.

The rate of solution in water of these salts is rapid, ten to fifteen minutes being ample time to obtain an almost quantitative solution with excess of hot water.

VI. LEACHING OF CALCINE

I. GENERAL NATURE OF WATER EXTRACT:

A water extract of calcined alunite will vary in colour and stability depending on the conditions of calcination and of extraction. The solution may be any shade from dark brown, through browns and yellows, to colourless; the gradual deposition of sediments will occur in all deeply coloured solutions, while the colourless extracts remain clear indefinitely.

The depth of colour is in some degree a pointer to the suitability of roasting conditions, a deeply coloured extract invariably indicating an incomplete roast, with the resulting undesirable concentration of aluminium (and to some extent, iron) in the extract. A clear extract, on the other hand, does not necessarily mean that suitable roasting conditions have been observed.

The following table (Table 17) gives some idea of the nature of the extracts obtained from a number of tests under varying calcination conditions but under roughly comparable extraction conditions.

Table 17. Nature of Water Extracts of Calcined Alunite

Calcination Conditions		Water Extract of Calcine		
Temp. °C.	Time min.	Colour	Al ₂ O ₃ % of calcine	Fe ₂ O ₃ % of calcine
600	45	dark brown	very heavy	n.d. *
700	20	"	"	"
700	60	"	1.85	"
750	20	brown	n.d.	"
750	45	deep yellow	"	"
750	90	yellow	"	"
800	8	brown	1.08	0.25
800	20	yellow	0.32	trace
800	30	colourless	nil	nil
800	15(a)	yellow	0.37	0.06
800	15(b)	brown	0.81	0.29
850	20	faint yellow	n.d.	n.d.
900	20	colourless	n.d.	n.d.

* n.d. not determined

(a) Rate of feed 1 cwt./hr.

(b) Rate of feed 2 cwt./hr.

From the table can be seen the gradation in colour of the extract from calcine obtained from tests in which the temperature of calcination alone was varied - the depth varies from dark brown in 600° and 700°C. extracts to colourless in the case of 850° to 900° roasts, the time of calcination in each case being 20 minutes. Increase in the time of calcination at the lower temperatures results in a decrease in colour intensity.

As would be expected from earlier work, the aluminium concentration in the extract decreases with higher temperatures or longer calcination periods, and thus decreases with decreasing depth of colour.

In general, a calcine which gives a deeply coloured solution on extraction with cold water will give a less deeply coloured extract on treatment with hot water. Boiling a coloured solution partially or completely decolourises it. The colour will be almost completely removed on grinding the cold extract with the calcine in a pebble mill for a period of 20 to 30 minutes.

The colour of these water extracts seems to be due mainly to the presence of colloidal iron, while the sedimentation resulting from long standing may be some form of basic alum gradually precipitating out.

The water extracts of the calcine from Calcination Tests 14, 15 and 16 (see Table 13) were, after several days standing, respectively brown and cloudy, yellow and slightly cloudy, and clear solutions. That from Test 14 was boiled and filtered, and the alumina and iron determined on the untreated extract, and on the filtrate and residue after boiling. The Al_2O_3 concentration in extracts 15 and 16 were also determined. Table 18 shows the results:-

Table 18. Al_2O_3 and Fe_2O_3 in Water Extracts.

Calcination Test No.	Treatment of Extract	Al_2O_3	Fe_2O_3	Al_2O_3	Fe_2O_3
		gm. per 100 ml. of extract		distribution per cent	
14	Untreated	.1518	.0334	100.0	100.0
	Boiled:-				
	(Filtrate)	.1252	.0036	82.4	10.8
	(Precipitate)	.0266	.0298	17.6	89.2
15	Untreated	.0442	trace	-	-
16	Untreated	.0012	nil	-	-

The results indicate that a large percentage of the iron content of an extract is precipitated, either as the hydrate or as a basic sulphate, on boiling, and also illustrate the extent to which the aluminium and iron concentrations fall off with increasing thermal decomposition of the ore.

2. STANDARD METHOD OF EXTRACTION FOR ANALYSIS:

The efficiency of a calcination test depends primarily on the percentage of the total K_2O content of the calcine which has been rendered water soluble by the calcination treatment.

To obtain this extraction figure a standard procedure was adopted. 70 gm. of calcine, unground in the case of all products grading minus 10 mesh, ground if coarser, were added to 200 ml. cold distilled water in a suitable beaker. The charge was placed on a hot plate and mechanically stirred with sufficient violence to keep the solids in suspension. After being extracted at boiling temperature for 15 minutes, with evaporation losses made up at intervals, the charge was allowed to settle and the supernatant solution passed through a filter. The insoluble residue was washed once by decantation and then transferred to the filter funnel, where it was treated with three 50 ml. hot water washes. The filtrate was made up to 500 ml. and aliquots taken for analysis.

This method of extraction was shown to recover over 99% of the total water soluble salts present in the calcine.

To determine the K_2O recovery from the calcine, a fusion of a sample was also necessary for determination of the total K_2O present.

Potassium analyses were made by the cobaltinitrite method. The method consists essentially of precipitating a complex sodium potassium cobaltinitrite, oxidising the precipitate with an excess of standard ceric sulphate solution and determining the excess ceric sulphate by titration with ferrous ammonium sulphate.

The method generally was satisfactory, but to obtain consistent results all analyses had to be made under rigidly controlled standard conditions.

3. LEACHING ALTERNATIVES:

The method adopted in practice for the extraction of the K_2SO_4 from the calcine would depend on a large number of factors, among which may be mentioned the necessity or otherwise for grinding the calcine, the feasibility of utilising the heat in the calcine at this stage, the settling and filtering properties of the ground and unground products, the ease of grinding of the calcine and the quantities of water available for leaching and washing.

As regards the first of these factors, even though unground calcine may yield up its water soluble potash as readily as the ground material, it may prove expedient to grind before extraction to enable certain types of equipment to be used which could not otherwise handle the material. What would be perhaps a more important consideration in this regard is the possibility of a ground potash residue being more acceptable than an unground material for the subsequent proposed alumina extraction process.

Consideration was given to four alternative leaching methods and flow sheets were suggested for each. These four alternatives were briefly:-

- (A) Extracting and washing the ground or unground calcine in a series of counter-current thickeners.
- (B) Extracting and washing the calcine in a series of counter-current rake classifiers.
- (C) Extracting and grinding the material in a ball mill, followed by thickening and filtration of the thickener underflow.
- (D) Leaching and washing the calcine by percolation in a counter flow series of vats.

Each of these alternatives will be discussed in detail, together with laboratory tests designed to determine the feasibility of the various stages in each.

All figures shown in the flow sheets assume the treatment daily of 214 tons of calcine which is an average figure for the amount of calcine to be treated to yield the proposed daily output of 30 tons of K_2SO_4 . The figures shown also assume a reduction, by washing or filtration, of the water soluble salts in the original ore from about 5% to 1% prior to calcination.

A. Leaching Alternative No. 1.

Use of Counter-current Thickeners:

This method involves the use of a series of counter-current thickeners and would depend to a large extent either on

- (i) the ability of thickeners to handle a quick and solid settling material such as would be discharged from the kiln, or
- (ii) the settling properties of a product ground to the sizing necessary for efficient handling by a thickener and to give the optimum extraction of potash and later, perhaps, of alumina.

From the settlement data available (see under Section B*4*) it is apparent that unless the percentage of slimes is kept very low, or unless the majority of the slimes can be overflowed from the first thickener and treated separately, the thickening area required for the handling of this material will be so great as to preclude entirely the use of counter-current thickeners for this purpose. The flow sheet is shown in Figure VIII.

(a) Ball Mill:

This unit would be included for either or both of the following reasons -

- (i) to reduce the sizing of the thickener feed should it prove impracticable to handle the unground material by thickeners and/or
- (ii) to grind the calcine should such a course result in an appreciable increase in the extraction of K_2SO_4 .

The effect of grinding the calcine on the subsequent potash extraction figure was determined experimentally. Calcine from Calcination Test 12 (see Table 13) was used, this test having been on -10-20 mesh material at 750°C. and a calcination period of 60 minutes.

Calcine samples were extracted with hot water, ground and unground, while a second series of extractions was made under identical conditions except that the extraction was carried out at room temperatures. The results are shown in the following table.

Table 19. Potash Extraction from Ground and Unground Calcine.

Leaching Test No.	Conditions of Extraction			Extract	
	Calcine sizing	Temper- ature °C.	Water Calcine	Total Salts % of calcine	K ₂ O extracted %
1	Unground	100	3 : 1	25.3	80.0
2	Ground	100	3 : 1	25.1	81.0
3	Unground	20	3 : 1	25.3	74.1
4	Ground	20	3 : 1	25.4	78.1

The figures show that when extraction is carried out at low temperatures, an additional 4% of K₂O is recovered by grinding the calcine prior to extraction; on the other hand, when leaching at temperatures approaching the boiling point, the extra recovery resulting from grinding is only 1% and is scarcely sufficient in itself to warrant the extra cost of grinding.

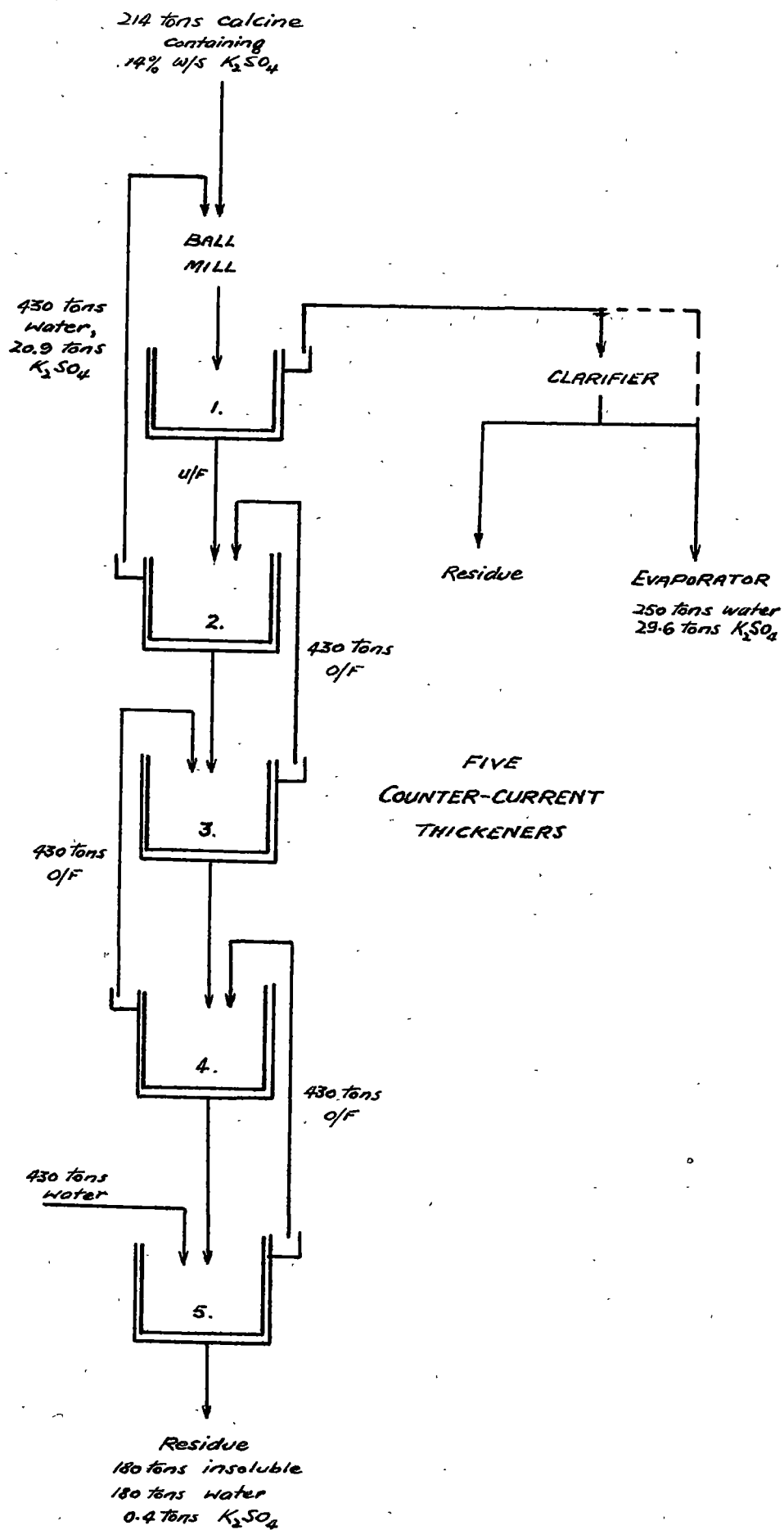


FIGURE VIII. LEACHING ALTERNATIVE NO.1 - COUNTER CURRENT THICKENERS.

A further series of grinding and extraction tests was carried out at room temperature, and under varying conditions of pulp density, fineness of grinding and time of extraction. The grinding was carried out in batches in porcelain Abbe mills, with calcine charges of 2 lb. and pebble loads of about 10 lb. The ball mill product was filtered in pressure filters, the filtrate analysed for K_2O and the filtration residue dried and graded.

Other tests in this series consisted of extracting in a mechanical agitator a sample of calcine ground dry to an arbitrarily chosen sizing. The extractions were made at two different pulp ratios and for increasing periods of time.

The conditions and results of this series are tabulated below (Table 20):-

Table 20. Potash Extractions under Varying Sizings, Pulp Ratios and Times.

Leaching Test No.	Water to Cal-cine	Grinding Time min.	Sizing Analyses of ground calcine									K_2O extraction %
			+20	+30	+40	+60	+80	+100	+150	+200	-200	
5(a)	Ball Mill Feed		7.4	61.4	25.9	3.0	0.6	0.7	0.4	0.1	0.5	-
5	1 : 1	5	-	0.7	4.3	7.6	3.7	9.3	15.2	3.0	56.2	61.8
6	"	10	-	-	0.2	1.1	1.2	4.8	12.1	3.5	75.1	60.9
7	"	15	-	-	-	0.1	0.2	1.7	6.1	2.8	89.1	61.7
8	"	20	-	-	-	-	0.1	0.7	3.2	1.8	94.2	60.2
9	2 : 1	5	-	2.3	8.7	7.9	4.6	9.6	12.2	3.1	51.6	70.5
10	"	10	-	0.1	1.3	3.4	2.9	7.0	11.3	4.5	69.5	70.1
11	"	15	-	-	0.2	0.9	1.2	3.8	11.0	2.9	80.0	70.5
12	"	20	-	-	0.1	0.3	0.7	2.8	8.6	2.8	84.7	71.4
		Extract-ing Time min.										
13	1 : 1	10)										62.9
14	"	20)										63.0
15	"	30)										63.6
16	2 : 1	10)	4.0	49.2	27.2	5.3	1.5	1.9	1.6	0.4	8.9	67.7
17	"	20)										68.1
18	"	30)										70.1

The conclusions to be drawn from the results shown in Table 20 are as follows:-

(i) that a pulp ratio of 1 part water to 1 part unextracted calcine does not give a maximum extraction in the cold, whereas a pulp ratio of 2 to 1 is sufficiently dilute to give a satisfactory extraction.

(ii) that extraction in the cold for periods of up to 30 minutes gives no better recovery of potash than short periods of 5 to 10 minutes.

(iii) that a calcine containing less than 10% minus 200 mesh fraction gives as good an extraction as one ground to over 90% minus 200.

They further indicate that, should grinding prior to thickening be practised, such grinding should be at a water to solids ratio approaching 2 to 1 to give a maximum extraction of the soluble potash before the calcine enters the washing system. This could best be achieved by returning a large percentage, if not the whole, of the overflow from No. 2 thickener to No. 1 thickener through the ball mill and not direct.

A comparison between the grindabilities of the calcine and a normal quartz ore are shown later under Leaching Alternative No. 3.

(b) Washing by Counter Current Decantation.

Settlement tests have shown that, whereas the unground calcine will settle to only little better than 50% solids, the fine minus 100 mesh fraction will not thicken beyond two of water to one of solids. It appears, therefore, that depending on the degree of grinding practised, it would be safer to regard the consistency of the underflow from the thickeners as being intermediate between these two figures.

The efficiency of the suggested system of five thickeners has therefore been calculated separately for each assumption, firstly, that a 1 to 1 pulp is discharged and secondly, that a $1\frac{1}{2}$ to 1 pulp is discharged.

- (i) For a 1 to 1 underflow: In this case it is assumed that 430 tons of fresh water are added to No.5 thickener every 24 hours and that 250 tons of concentrated K_2SO_4 solution are overflowed from No.1 thickener in the same period.

The following relationships are obtained by equating the tons of K_2SO_4 into and out of each thickener:-

$$\begin{array}{rclclcl} 30 & + & 430 B & = & 180 A & + & 250 A & = & 430 A. \\ 180A & + & 430 C & = & 180 B & + & 430 B & = & 610 B. \\ 180B & + & 430 D & = & 180 C & + & 430 C & = & 610 C. \\ 180C & + & 430 E & = & 180 D & + & 430 D & = & 610 D. \\ 180D & & & = & 180 E & + & 430 E & = & 610 E. \end{array}$$

where A, B, C, D, E represent the tons of K_2SO_4 per ton of water in thickener Nos. 1, 2, 3, 4, 5, respectively, and where 180 represents the tons of insoluble residue resulting from the leaching of 214 tons of calcine.

Solving these equations, we obtain the following values for the unknowns:-

A	0.11846
B	0.04869
C	0.01949
D	0.00726
E	0.00214

These figures show that the use of 4 counter current decantation thickeners would result in the loss of approximately $180 \times 0.00726 = 1.31$ tons of K_2SO_4 per 24 hour day, while the addition of a fifth unit would reduce this figure to 0.39 tons.

- (ii) For a $1\frac{1}{2}$ to 1 under-flow: Here it will be necessary to add 520 tons of fresh water per 24 hours to the system while the discharge from each thickener will carry 270 tons of solution instead of the 180 tons above.

The equations will now become:-

$$\begin{array}{rclclcl}
 30 & + & 520 & B & = & 270A & + & 250A & = & 520 & A \\
 270A & + & 520 & C & = & 270B & + & 520B & = & 790 & B \\
 270B & + & 520 & D & = & 270C & + & 520C & = & 790 & C \\
 270C & + & 520 & E & = & 270D & + & 520D & = & 790 & D \\
 270D & & & & = & 270E & + & 520E & = & 790 & E
 \end{array}$$

giving the following values for the concentrations in each thickener:-

A	0.11548
B	0.05779
C	0.02783
D	0.01247
E	0.00426

In this case, therefore, the loss of K_2SO_4 per day from a system of five units is 1.15 tons.

(c) Clarification of No. 1 Thickener Overflow:

This would be necessary only if it were decided to overflow a cloudy solution in order to save thickening area. If a clear overflow were required, the slow settling rate of the fine fractions of the calcine would necessitate considerable thickening area and whether or not clarification would be necessary would depend to a large extent on such factors as -

- (i) tonnage of fines to be settled,
- (ii) the balance between cost of clarifying and cost of extra thickening area required to give a clear overflow.

Whether ordinary sand clarifiers would suffice or whether some form of mechanical unit would be necessary would depend on the tonnage and nature of suspended matter overflowing No. 1 thickener.

B. Leaching Alternative No. 2.

Use of Counter-current Classifiers:

The use of a series of counter-current classifiers for the leaching of the calcine would enable the material to be treated without preliminary grinding, thus reducing to a minimum the quantities of slow settling and not easily filterable fines to be thickened and filtered at a later stage.

In a system of counter-current thickeners handling a slow settling and partially ground product the solids are, of necessity, stored under water for a considerable period. In the case of rake or helical classifiers handling a coarse, unground feed this long period of contact is avoided.

The sliming effect produced in a ground calcine pulp after prolonged standing was shown by grinding a 1 to 1 mixture for 10 minutes, sampling the pulp, allowing to stand for 72 hours and re-sampling. Sizing analyses of the two samples gave the following figures (Table 21).

Table 21. Ground Calcine Pulps.

I.M.M. Screen	Aperture m.m.	Weight per cent	
		After 10 Minutes	After 72 Hours.
+ 30	0.423	0.6	0.2
+ 40	0.317	3.9	2.2
+ 60	0.211	8.6	5.6
+ 80	0.157	5.0	4.4
+ 100	0.127	11.3	10.0
+ 150	0.084	15.7	13.2
+ 200	0.063	3.1	4.3
- 200	-	51.8	60.1

Thus the use of classifiers would seem to be preferable in this respect at least to the use of counter-current thickeners.

The system is represented diagrammatically in Figure IX.

(a) The Use of Classifiers for extraction and washing of K_2SO_4 from Calcine.

The choice of six classifiers is purely arbitrary but by the application of principles similar to those applied in the case of the counter-current thickeners, it appears that six units would give a final residue carrying less than 0.5 tons soluble K_2SO_4 per 24 hours. This is based on the fact that the same weight of calcine is washed by approximately the same quantity of water in the same time and on the assumption that the sand from each classifier contains at least 50% insoluble solids. This latter assumption is justified by experimental settling tests, and by the fact that the water to solids ratio in the discharged sands could be appreciably decreased by additional draining area in the final unit and still further by some form of mechanical vibration.

Though rake classifiers are shown on the tentative flow-sheet, consideration could be given to the possibility of a series of helical type machines. As it is desired to keep the amount of fines in the system at a minimum, a factor influencing the choice of machines would be their effect on the sizing of the material during its passage through the series, and, in this respect, the Akins type would perhaps be preferable to rake classifiers.

It would be advantageous to add the hot calcine direct to the classifiers from the furnace, and it is possible that its addition to the well of an ordinary rake or helical classifier would set up undesirable convection currents, causing perhaps the overflow of unduly dilute solution to the press or thickeners. Feeding to some type of bowl classifier would, to a great extent, obviate this difficulty.

As regards the addition of the hot calcine to cold water, it has been shown in the laboratory that the average specific heat of the material between $500^{\circ}C.$ and $25^{\circ}C.$ is 0.245 calories per gram, which indicates roughly that one ton of calcine at $400^{\circ}C.$ would raise its own weight of water to boiling.

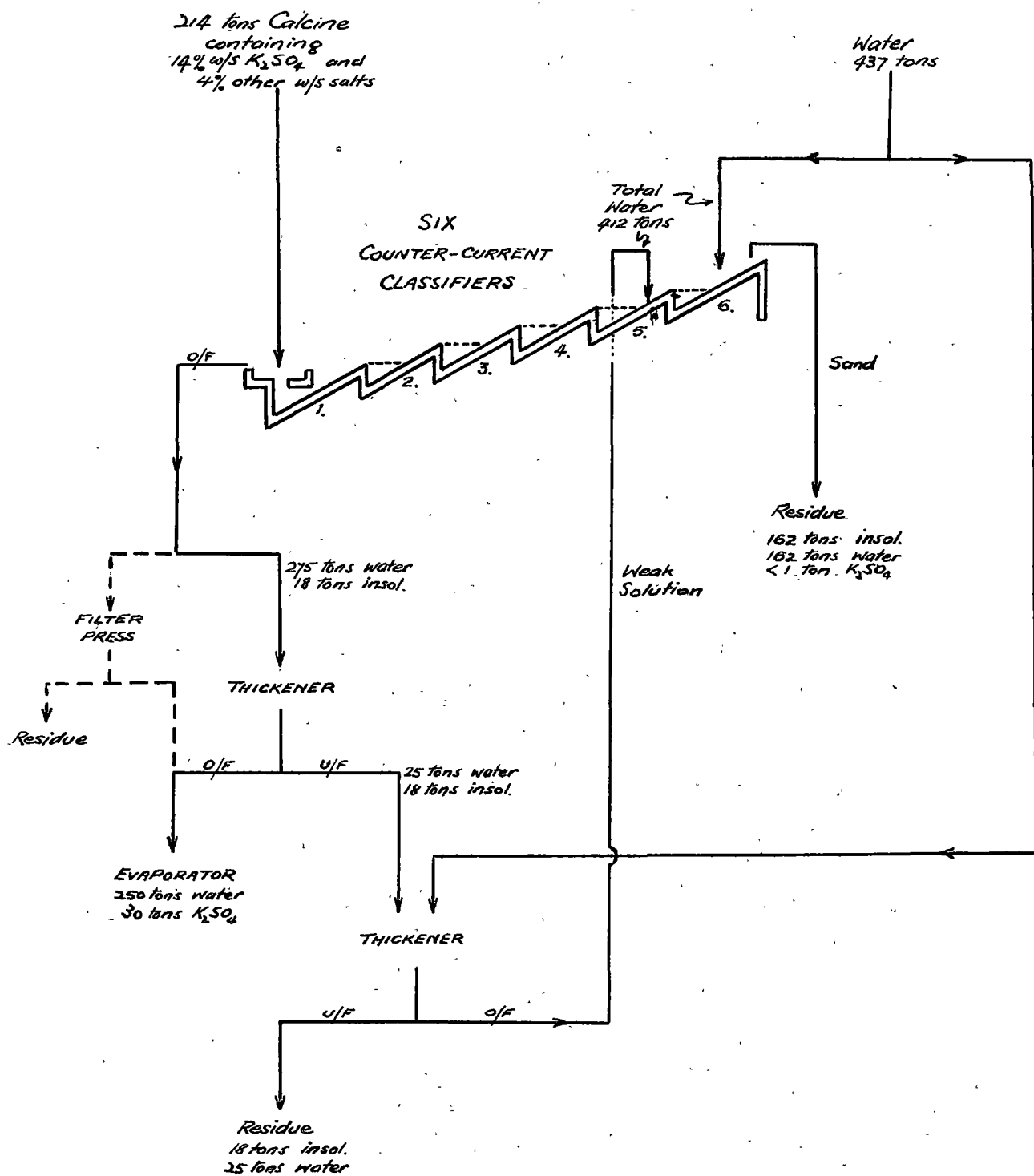


FIGURE IX. LEACHING ALTERNATIVE NO. 2 - COUNTER CURRENT CLASSIFIERS.

A roughly quantitative experiment has been described (V.2 D (i)) in which it is shown that less than 1% of minus 200 material is produced by the addition of hot calcine (about 700°C.) direct to water.

(b) Treatment of the Classifier Overflow:

All tonnages shown in this and the preceding section are calculated on the assumption that 10 per cent of the insoluble solids fed to the system overflow with the concentrated solution from No. 1 classifier. Thus it is assumed that 18 tons of fines per 24 hours are to be handled (214 tons calcine fed to system, which contain 14% or 30 tons K_2SO_4 + 4 tons other water soluble salts, leaving 180 tons insoluble).

From the experiment referred to in the last paragraph of section (a) above, it is apparent that the amount of fines due to shattering when the hot calcine first contacts the cool water would not be more than 1 ton per 24 hours, assuming, of course, a furnace discharge with normal quantities of finer fractions.

The sizing analysis shown in Leaching Test 15 (Table 20) is of a product resulting from a rather violent agitation for 30 minutes at a pulp ratio of 1 calcine to 1 water of the material grading as shown in Leaching Test 5(a). This treatment increased the -100 fractions from 1.0% to 10.9% and the -200 fractions from 0.5% to 8.9%.

The relatively mild agitation obtained in a classifier considered in conjunction with the above experimental figures, would indicate that the estimated overflow of 10% insoluble solids is likely to be in excess of, rather than below, the true figure.

Two alternative treatments for the overflow are shown on the flowsheet, consisting of -

- (i) two thickeners, connected counter-current, but in series with the classifier units, and
- (ii) a filtering unit.

(i) Thickening:

As regards thickening, the settlement rate, though normally slow, would be accelerated slightly as the temperature of the solution at this stage would still be considerably above atmospheric temperature. The high solution to solids ratio of 2 to 1 in the final discharge would be offset by the small tonnages to be handled and the consequent possibility of very high solution to solids ratio during washing in the two thickeners. This assumption that the discharge ratio would be 2 to 1 would give a reasonable safety margin and would result in a final discard from the second thickener of approximately 36 tons of water per day.

To determine the dimensions of the thickener required to handle 18 tons per day of minus 100 mesh calcine, a number of settlement tests were carried out in concentrated solutions of K_2SO_4 . From these experiments the values of R (see Section IV,2) were obtained for corresponding values of F (the weight of water to 1 part, by weight, of solids at a given dilution) and the area required (A) per ton of solids per 24 hours estimated from the equation

$$A = \frac{1.493 (F-D)}{R}$$

The tests were carried out at two different temperatures, namely 19°C. and 50°C., and under the following conditions:-

Sizing of Calcine	-100 + 200	13.5%
	- 200	86.5%
Specific Gravity of Leached Calcine	2.86	
Dry weight of leached calcine	170 grams.	
Volume occupied by leached calcine	60 c.c.	
Soluble salts per 100 ml. of solution	8.5 grms at 19°C.	
	14.2 " " 50°C.	

During free settling the rate of settlement was determined by taking pulp level readings at 3 minute intervals for a quarter of an hour. The appearance of channels in the pulp at a pulp ratio of 3 : 1 indicated that compression settlement had started at this dilution.

The results of the free settling tests are set out in Table 22.

Table 22. Free Settlement of Minus 100 Mesh Calcine.

F	R		D	(F-D)	1.493 (F-D)	A	
	ft./hr.					sq.ft./ton/24 hr.	
	19°	50°				19°	50°
3	.019	.017	2	1	1.49	78	88
4	.038	.030	"	2	2.99	79	100
5	.038	.041	"	3	4.48	118	109
6	.052	.049	"	4	5.97	115	122
7	.052	.065	"	5	7.47	144	115
8	.057	.060	"	6	8.96	157	149
9	.057	.076	"	7	10.45	183	138
10	.063	.076	"	8	11.94	190	157
11	.079	.090	"	9	13.44	171	149
12	.083	.098	"	10	14.93	180	152
14	.100	-	"	12	17.92	179	-

These figures show that the minimum allowable area for settlement is 190 sq. ft. per ton per 24 hrs. at 19°C. and 157 sq. ft. at 50°C. The figure D = 2 is used in making the above calculations; actually D = 2.07 is the figure obtained in the following hindered settlement tests.

Compression settlement tests enabled the depth of the thickener to be calculated. Owing to the difficulty of maintaining the pulp at 50°C. for a period of over 24 hours, this test was made only at 19°C. After compression settlement had commenced in the free settlement test pulp above, the pulp was very gently stirred after each hourly pulp line reading had been taken and the corresponding pulp ratio then calculated.

Results are shown in Table 23.

Table 23. Compression Settlement of Minus 100 Mesh Calcine.

Reading of pulp line a c.c.	Volume of Solution (a-60) c.c.	Dilution Gr.Soln:1 solids a - 60 170	Time interval t hours	Corres- ponding average dilution d.	d x t
590	530	3.12			
584	524	3.08	1	3.10	3.10
577	517	3.04	1	3.06	3.06
571	511	3.01	1	3.03	3.03
563	503	2.96	1	2.99	2.99
555	495	2.91	1	2.94	2.94
545	485	2.85	1	2.88	2.88
518	458	2.69	2½	2.77	6.92
456	396	2.33	4	2.51	10.04
417	357	2.10	9½	2.22	21.10
415	355	2.09	1	2.09	2.09
415	355	2.09	1	2.09	2.09
414	354	2.08	1	2.08	2.08
413	353	2.08	1	2.08	2.08
412	352	2.07	1	2.07	2.07
		Total	27		66.47

Hence the average dilution in the compression zone

$$= \frac{66.47}{27} = 2.46$$

and average specific gravity of pulp in this zone

$$= \frac{2.46 + 1}{\frac{2.46 + 1}{2.86}} = 1.23$$

Also

Final density - solids to 1 part solution = 2.07

Hours retention necessary to reach this density ... = 24

Sq.ft./ton of solids/24 hrs. (a) at 19°C. = 190

(b) at 50°C. = 157

Capacity in lb. dry solids/sq.ft./hr.

$$(a) \text{ at } 19^{\circ}\text{C} = \frac{2240}{24 \times 190} = 0.49$$

$$(b) \text{ at } 50^{\circ}\text{C} = \frac{2240}{24 \times 157} = 0.59$$

To hold these quantities/sq.ft./hr. for 24 hours will mean storage for

$$(a) 24 \times 0.49 = 11.8 \text{ lb. solids} = 40.8 \text{ lb. pulp/sq.ft./hr.}$$

$$(b) 24 \times 0.59 = 14.2 \text{ lb. solids} = 49.1 \text{ lb. pulp/sq.ft./hr.}$$

Hence depth of compression zone is

$$(a) \frac{40.8}{62.5 \times 1.23} \text{ feet} = 0.53 \text{ ft.}$$

$$(b) \frac{49.1}{62.5 \times 1.23} \text{ feet} = 0.64 \text{ ft.}$$

With these figures available we can now determine the required thickener dimensions, as follows:-

	<u>At 19°</u>	<u>At 50°</u>
Solids to be handled per 24 hrs - tons	18	18
Area required (from test work) sq.ft./ ton/24 hr.	190	157
Area added for emergencies (say 10%)	19	16
Area recommended - sq.ft./ton/24 hr.	209	173
Total area recommended - sq. ft.	3762	3114
Diameter of thickener - ft. ...	69	63
Assume slope of raking arms in thickener - in/ft.	1½	1½
Maximum depth of arms - ft. ...	3.59	3.28
Assume 2/3 of this depth ineffective due to solids building up under the rakes: so ineffective depth - ft.	2.39	2.19
Total depth of thickener -		
Ineffective	2.39	2.19
Compression zone	0.53	0.64
Feed well	2.00	2.00
<u>Total</u>	<u>4.92</u>	<u>4.83</u>

Thickener Required: Diameter x depth - ft.
69 x 5 63 x 5

The above thickener dimensions seem out of all proportions to the tonnage of material handled, and constitute perhaps the best argument in favour of filters for the dewatering of these slimes.

As in the case of the wash from the filter, the overflow from the second thickener would rejoin the leaching circuit late in the washing stage. Fresh water, including the weak solution from this source, would be added to the leaching circuit at the rate of 412 tons per 24 hours.

(ii) Filtering:

Filtering tests indicate that the dewatering of these fines by filtration would be slow. In pressure filtering even granular calcine (over 95% # 60 mesh and less than 1% - 200 mesh) the very thin layer of slimes which settles on top of the cake results in an early and marked slowing down in the filtering rate. However, with only small tonnages to be handled and the better mixing of these fines under large scale filtering conditions, it appears that the possibilities of filtration at this stage should be given every consideration.

As regards the actual type of filtering unit used, it is considered improbable that an ordinary rotating drum type vacuum filter would be practicable, owing mainly to the poor cake formation and to the difficulties of washing efficiently. Types which seem to present possibilities in this respect are pre-coat vacuum filters and chamber presses with recessed plates.

The wash from the filter would be returned to the circuit at the appropriate point in the leaching system.

A number of filtration tests were made to determine the filtration characteristics of an average classifier overflow.

Samples for test work were obtained by moderate agitation with water of approximately 100 lb. of mixed calcines resulting from 750°C. and 800°C. roasts, and classifying off the resultant slimes.

The quantity of slimes so obtained was of the order of one percent of the calcine treated. The calcine and the water were both cold and the agitation was necessarily such that very little abrasive action took place. In actual practice, the ratio of insoluble solids in the classifier overflow to the insoluble solids in the feed will depend largely on the nature of the furnace discharge and on the adjustment of the overflow weir and other factors which may be controlled at the will of the operator.

A sizing analysis of the insoluble solids in the pulps used for the test work showed 0.5% minus 100 plus 200 mesh, and 99.5% minus 200 mesh.

As in previous filtration experiments in which Leaf C (described in IV, 1, previously) was used, four types of filter cloth were available (calico, 10 oz., 15 oz. and 17½ oz. duck respectively), while the effective area of the test leaf was 0.1 sq. ft.

In all tests, the liquid portions of the pulp consisted of a solution of the salts present in calcine from unwashed furnace feed, chiefly potassium, sodium and magnesium sulphates. The concentration of these salts varied from approximately 11.0 gr per 100 c.c. solution down to 7.5 gr. per 100 c.c. in some cases.

From the results of the work may be compared the suitability of the various filter media, the effects of temperature and pulp ratio on the filtering properties of the fines and the efficiency of washing under different conditions.

(iia) Suitability of Various Filter Cloths:

Some slight increase in density of a pulp is to be expected after a series of filtration tests, due chiefly to local thickening where the pulp is in contact with the cake - a thickening which has not gone far enough actually to form cake.

To obviate this inconsistency a pulp sample was divided into four identical samples and the following tests carried out each on a fresh sample of pulp.

Constant conditions:-

Pulp ratio	15.5 solution to 1 insoluble solids
Temperature	19°C. (66.2 F)
Salts in solution	7.52 gr. per 100 c.c.
Cake forming	180 seconds.
Cake drying	60 seconds.
Cake thickness	1/16th inch approx.
Filter area	0.1 sq. ft.
Vacuum	26 inches.

Table 24. Calcline Filtration using Various Filter Cloths.

Filter Test No.	Cloth	F i l t e r C a k e				
		Wet gr.	per cent Moisture	Dry unwashed gr.	per cent Soluble	Insoluble gr.
62	10 oz.duck	25.1	48.2	13.0	7.3	12.1
63	15 " "	24.4	48.8	12.5	7.6	11.6
64	17½ " "	24.3	49.4	12.3	7.7	11.3
65	Calico	24.8	48.8	12.7	7.7	11.7

These results indicate that the 10 oz. cloth will give a higher filtration rate than any of the other materials tested, the insoluble cake weight obtained when using this material being 7.1% greater than when using the slowest filtering medium, viz. 17½ oz. duck.

(iib) Effect of Washing:

These tests were made under the conditions and with the results shown in the following table :-

Constant Conditions:-

Pulp ratio 15.5 to 1
 Temperature 18°C. (64.4°F.)
 Salts in solution 11.0 gr. per 100 c.c.
 Cake thickness 1/16th inch approx.
 Filter medium 17½ oz. duck
 Filter area 0.1 sq. ft.
 Vacuum 26 inches.

Table 25. Calcline Filtration - Effect of Washing.

Filter Test No.	C y c l e - s e c.				Fil- trate c.c.	Wash c.c.	C a k e			Salts discard- ed per 24 hr. tons.
	Cake form- ing.	Drain- ing	Wash- ing.	Dry- ing			Mois- ture	Dry cake		
								wt. gr.	% soluble	
66	180	10	300	60	236	380	57.0	10.2	0.84	0.15
67	180	10	95	60	230	115	56.3	10.4	1.17	0.21
68	180	-	-	60	230	-	51.7	11.7	11.76	2.40

In the use of classifiers for leaching, it is proposed that 437 tons of water enter the system per 24 hrs. while 250 tons go to the evaporator as filtrate (or thickener overflow). It would therefore be possible to wash the slimes on the filter with 437 tons of water without introducing further water into the system. Thus the maximum ratio of filtrate to wash would be 250 to 437 and these conditions have been approximated in test 66 above. To wash with this amount of water required as washing time 1.7 times the cake forming period.

The last column in the above table is calculated assuming 18 tons of slimes per day, and under the test conditions, includes sodium and magnesium salts as well as potassium sulphate.

(iic) Effect of Temperature:

Filtration tests carried out at different temperatures gave the following results:-

Constant Conditions:-

Pulp ratio	11 to 1
Salts in solution	7.5 gr./100 c.c.
Filter medium	17½ oz. duck
Cake forming	180 seconds
Draining	45 "
Cake washing	100 "
Cake drying	60 "
Filter area	0.1 sq. ft.
Vacuum	26 inches.
Temperature of wash water	19°C.

Table 26. Calcine Filtration - Effect of Temperature.

Filter Test No.	Temp. °C.	Filtrate c.c.	Wash c.c.	Filter cake					
				Approx Thick-ness inch	Wet Weight gr.	Mois-ture %	Dry weight gr.	Sol-uble %	Insol-uble gr.
69	20	170	80	1/16	22.8	51.3	11.1	1.10	11.0
70	55	215	40	1/8	42.5	51.1	20.8	1.35	20.5
71	90	220	40	1/6	47.3	51.2	23.1	1.62	22.7

These results show that by filtering at 90°C. the insoluble filter residue is 106% greater than that obtained when the process is carried out at atmospheric temperatures.

In addition, the cake blows away from the cloth more cleanly and the filtrate is appreciably clearer at the higher temperature. Against this, there seems to be a need for longer washing periods at higher temperatures to obtain equal elimination of soluble salts.

(iid) Effect of Pulp Ratio:

Tests were made on pulps of different densities. The pulp ratio is expressed as parts by weight of solution to parts by weight of insoluble solids. Following are the conditions and results of these tests:-

Constant conditions:-

Temperature	19°C. (66.2°F)
Salts in solution	7.5 gr. to 10.5 gr./100 c.c.
Filter medium	17½ oz. duck
Cake forming	180 seconds
Draining	20 "
Cake washing	95 "
Cake drying	60 "
Filter area	0.1 sq. ft.
Vacuum	26 inches.

Table 27. Calcine Filtration - Effect of Pulp Ratio.

Filter Test No.	Pulp ratio	Filtrate c.c.	Wash c.c.	Filter Cake					
				Thick-ness in.	Wet Weight gr.	Mois-ture %	Dry Weight gr.	Sol-uble %	Insol-uble gr.
72	32:1	235	115	1/32	11.2	55.4	5.3	0.87	5.3
73	15½:1	230	115	1/16-	21.2	52.0	10.2	1.17	10.1
74	11:1	170	80	1/16+	22.8	51.3	11.1	1.10	11.0
75	8:1	166	90	1/8	27.7	56.3	12.1	1.20	12.0

Figure X has been drawn from the data contained in the foregoing table. From this graph may be determined the approximate cake weights per square foot to be expected at various dilutions of pulp.

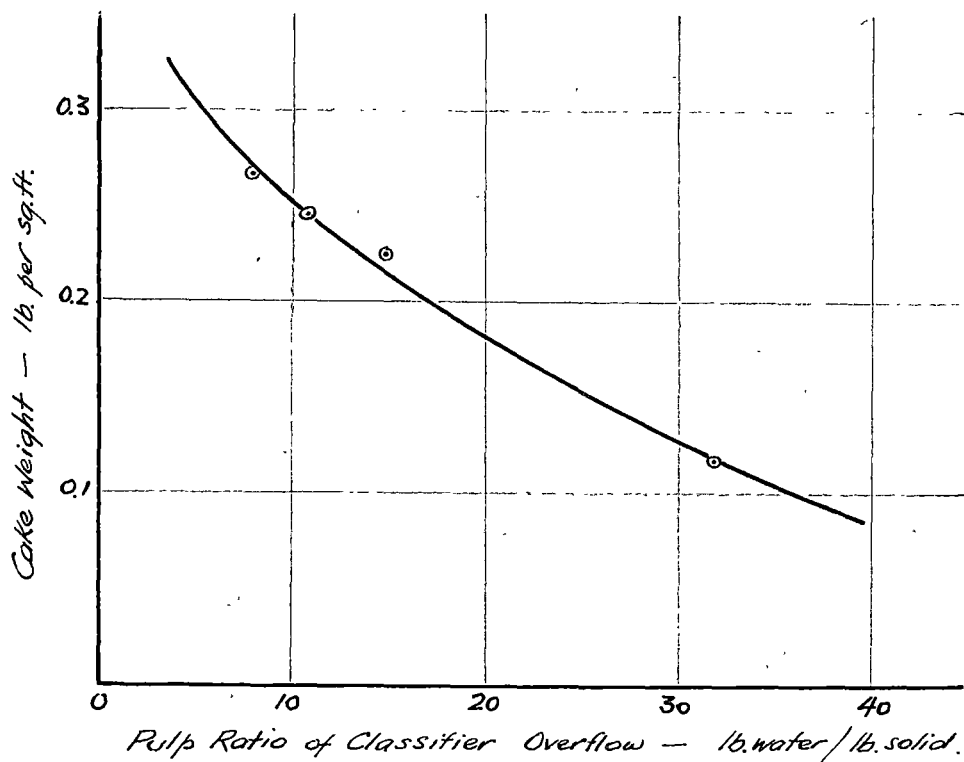


FIGURE X. RELATIONSHIP BETWEEN FILTER CAKE AND PULP RATIO.

Using the figures obtained by interpolation from Fig.X and those obtained in the preceding section (see Table 26), the following table (Table 28) is drawn up showing the relationship between the filter areas required at different dilutions of the classifier overflow and at different temperatures of filtration.

The assumptions made are:-

Insoluble in feed to classifiers	180 tons
per 24 hours	
Solution to evaporators per 24 hrs.	250 tons.
Rotating drum filtration cycle	7½ mins.
Moisture in filter cake	50 per cent.

Table 28. Calcine Filtration - Relation between Pulp Ratio and Filter Area Required.

% of insol- uble classifier feed in O/F	Insol- uble solids in O/F a tons	Pulp ratio of O/F $\frac{250}{a}$	Insol- uble filter cake b lb/sqft	Filter area required A sq.ft. $A = \frac{a}{b} \times \frac{11.66}{0.7}$		
				20°C.	55°C.	90°C.
4	7.2	34.7	.097	1237	664	600
5	9.0	27.8	.137	1094	587	530
6	10.8	23.1	.165	1089	584	527
7	12.6	19.8	.185	1134	609	550
8	14.4	17.4	.201	1194	641	579
10	18.0	13.9	.223	1344	721	651
12	21.6	11.6	.236	1523	817	739
14	25.2	9.9	.243	1729	927	839

The filter area required has been adjusted for possible cover blinding, it having been assumed that the efficiency of the filter cloth will be reduced from this cause by 30%.

The figures for the areas required at 55° and 90°C. were obtained by multiplying the areas required at 20°C. by 0.537 and 0.485, respectively, these factors being obtained from the results of tests 69-71.

The factors used in compiling the above table are necessarily fairly wide approximations, but the results are of interest mainly for purposes of comparison.

From the graph obtained by plotting the percentage of insoluble classifier feed appearing in the classifier overflow against the filtering area required to handle the resultant tonage of fines (Figure XI) can be found the most favourable balance between these two variables.

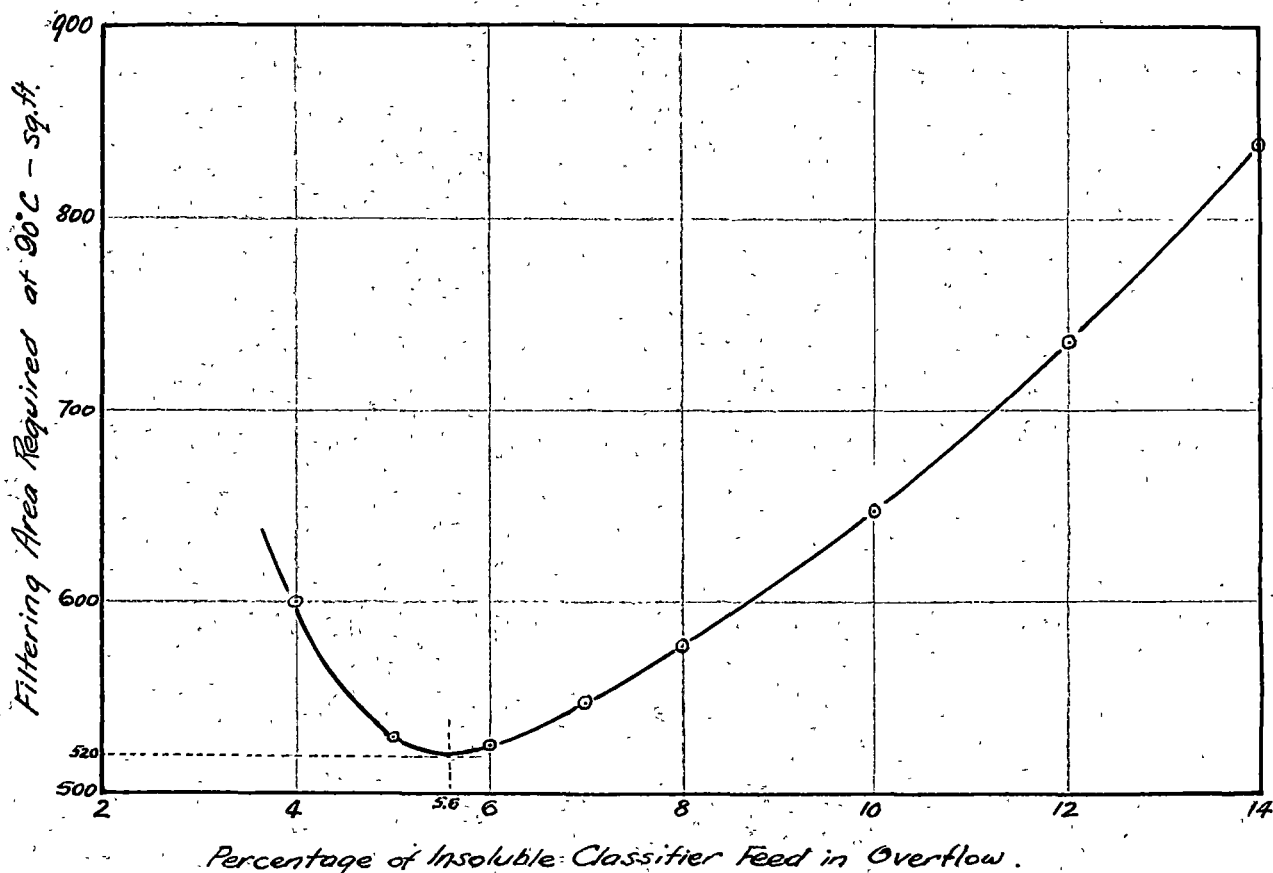


FIGURE XI. RELATIONSHIP BETWEEN FILTER AREA AND PULP RATIO.

Thus it is found that the latter is a minimum at 520 sq. ft. when filtration is carried out at 90°C. and when 5.6 per cent of the insoluble classifier feed overflows with the pregnant solution. The ratio of solution to solids in the overflow is, under these conditions, of the order of 25 to 1.

(iie) Rate of Increase of Filter Cake:

Though there is much to be said for the continuity of operation resulting from the use of rotating drum vacuum filters, the use of these machines for handling this type of pulp may be somewhat limited in this case, mainly by the high dilution and slow rate of cake formation.

Even when filtering at 90°C., the maximum cake thickness obtained in 3 minutes was between 1/8 inch and 3/16 inch, while assuming that a 5 minute cake forming period could be allowed, the maximum cake thickness that could be expected would be little more than 3/16 inch.

A factor which would lessen the difficulty of discharging such a cake is the readiness with which it can be blown off the filter cloth. A cake formed by hot filtration discharged more cleanly than one formed in the cold.

A test (Filter Test 76) has been carried out to obtain figures which would be of use should consideration be given to the possibility of using vacuum-leaf filters for this work.

Filtration was continued for 30 minutes in a pulp of initial ratio 16 solution to 1 insoluble solids, and the volume of filtrate measured at two minute intervals.

The constant conditions during the test were:-

Filtering medium	10 oz. duck
Filter area	0.1 sq. ft.
Temperature	19°C. (66.2°F)
Salts in solution	11.0 gr. per 100 c.c.
Vacuum	26 inches.

The results were as shown in Table 29.

Table 29. Calcine Filtration - Rate of Increase of Filter Cake.

Filter Cake	
Thickness	0.2 inch.
Moisture	50.7 per cent.
Wet unwashed - weight	70.3 grams.
Dry unwashed - weight	34.7 grams.
- per cent soluble	10.6 per cent.
Dry insoluble - weight (calcd.)	31.0 grams.

Time Inter- vals mins.	Fil- trate A c.c.	Dry unwash- ed cake B = A x $\frac{34.7}{766}$ gm.	Dry unwash- ed cake C=Bx0.022 lb/sq.ft.	Insoluble cake	
				D=Cx0.894 lb/sq.ft.	Rate of increase lb/sq.ft/min.
1	147	6.66	0.15	0.13	0.131
2	198	8.97	0.20	0.18	0.046
3	242	10.97	0.24	0.22	0.040
4	270	12.24	0.27	0.24	0.025
6	329	14.90	0.33	0.29	0.026
8	382	17.32	0.38	0.34	0.024
10	426	19.31	0.43	0.38	0.020
12	479	21.70	0.48	0.43	0.023
14	519	23.52	0.52	0.46	0.018
16	556	25.19	0.56	0.50	0.016
18	589	26.70	0.59	0.53	0.015
20	623	28.22	0.62	0.56	0.015
22	652	29.60	0.65	0.58	0.014
24	683	30.95	0.68	0.61	0.013
26	715	32.40	0.71	0.64	0.014
28	738	33.45	0.74	0.66	0.010
30	766	34.70	0.76	0.68	0.012

The results show a fairly steady decrease in filtering rate after the first three minutes.

Allowing a 30 minute cake forming period it is reasonable to assume say a 90 minute cycle. Thus during each cycle a cake would form containing 0.68 lb. insoluble residue per square foot of filtering area and the total filtering area required to handle t tons of fines per 24 hours would be given by

$$A = \frac{2240 \times 1.5}{0.68 \times 24} t \quad \text{sq. ft.}$$

$$= 206 t \quad \text{sq. ft.}$$

If filtering were carried out at 90°C. instead of at atmospheric temperature - and in practice a filtration temperature approaching 90°C. may reasonably be expected - then from Filter Test Nos. 69 and 71, the value of A under these conditions would be -

$$A = \frac{11.1}{23.1} \times 206 t \quad \text{sq. ft.}$$

$$= 99 t \quad \text{sq. ft.}$$

$$= 178 p \quad \text{sq. ft.}$$

where p is the percentage of insoluble classifier feed which overflows as slimes.

Allowance must be made for the effect of the gradual clogging action of the slimes on the efficiency of the filter cloth, and so, assuming a cover-blinding factor of 0.7, the above area would, under plant operating conditions, become -

$$A = 141 t = 254 p \quad \text{sq. ft.}$$

These figures apply, of course, only to filtration at pulp ratios of the order of 16 to 1. Some idea of the approximate areas required at other dilutions may be obtained from a consideration of the results of tests 72-75.

C. Leaching Alternative No. 3

Thickening and Filtration of Ball-mill Product:

This method involves the use of thickeners and vacuum filters to wash and dewater the ground calcine.

In filtration tests carried out on the ground calcine (see below, Filter Tests Nos. 77-78), under conditions representing a normal Oliver filter cycle, a cake was obtained carrying about 38% moisture and 16.3% of residual water-soluble salts. Considering that the unwashed calcine contains only 26.6% of water-soluble salts these results indicate that vacuum filtration of the calcine could be satisfactorily conducted only if double filtration with intermediate repulping and thickening were practised.

Figure XII illustrates a possible flow sheet for this method of leaching.

(a) Ball Mill:

Grinding of the calcine should present no difficulties. Four tests were conducted whereby figures were obtained comparing the general grinding characteristics of the calcine with those of a clean quartz ore.

The quartz ore was stage ground through a Braun pulveriser, the various fractions sieved out, and a synthetic product was made up from the various fractions to give a sizing analysis identical with that of the unground calcine.

One pound charges were added with the same weight of water to Abbe pebble mills carrying pebble loads of 9 lb.

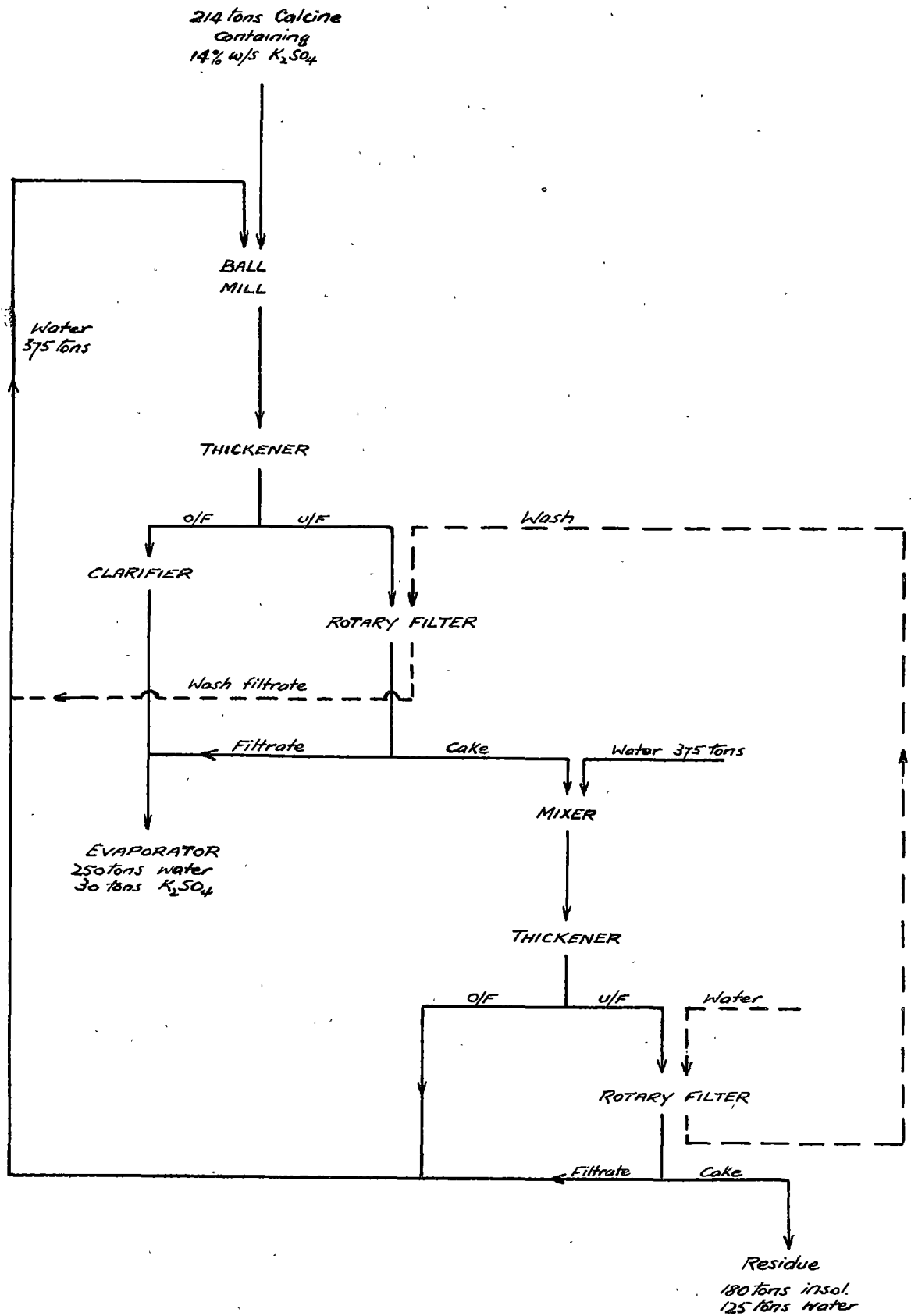


FIGURE XII. LEACHING ALTERNATIVE NO.3. - GRINDING, THICKENING AND FILTERING.

each. Grinding was allowed to proceed for 15 and 30 minutes, after which the sizings of each product was determined. The results are shown in Table 30.

Table 30. Grinding of Calcine.

I M M Screen	Sizing Analyses - per cent				
	Initial Sizing	After 15 minutes		After 30 minutes	
		Quartz	Calcine	Quartz	Calcine
+ 20	7.4	0.4	-	-	-
+ 30	61.4	18.2	0.4	1.1	-
+ 40	25.9	16.3	4.7	3.5	-
+ 60	3.0	13.1	5.1	5.0	0.1
+ 80	0.6	5.8	4.9	3.5	0.1
+100	0.7	10.1	12.7	11.6	2.9
+150	0.4	11.7	13.3	24.1	11.1
+200	0.1	3.6	3.5	5.8	3.5
-200	0.5	20.8	55.4	45.4	82.3

(b) First Thickener:

Owing to the relatively poor filtering properties of the ground calcine, this thickener would serve a useful purpose in taking much of the load from the rotary filter.

Assuming the overflow to be of the order of 100 tons solution per day, the thickener underflow fed to the filter would have a consistency of approximately 40% solids, this latter figure depending to a large extent on the fineness of grinding. The overflow, together with the filtrate from the first filter, would constitute the evaporator feed.

(c) First Rotary Filter:

This unit should give as filter cake 180 tons of insoluble residue per 24 hours, together with approximately 125 tons of water carrying 15 tons of K_2SO_4 . Assuming settlement to a $1\frac{1}{2}$ to 1 pulp ratio in the first thickener then the feed to the filter would be 455 tons of pulp in addition to 33 tons of dissolved K_2SO_4 per day.

The filter cake would next be repulped for washing with fresh water at as high dilution as practicable, say by the addition of 375 tons of water, giving a pulp ratio of the order of 2.8 water to 1 insoluble solids in the mixer.

It seems questionable whether washing on the first filter would be good practice, as greater benefit would be derived by introducing what additional water can be added to the circuit at the mixer.

Filter Tests Nos. 77 and 78 were carried out on a calcine pulp wet ground to the following sizing:-

<u>Fraction</u>	<u>Weight %</u>
+ 30	0.6
+ 40	3.9
+ 60	8.6
+ 80	5.0
+ 100	11.3
+ 150	15.7
+ 200	3.1
- 200	51.8

The result of the tests indicated that a 3/16" cake would be obtained during a three minute cycle. The dry weight of the cake per sq. ft. averaged 0.75 lb. but as this contained 16.3% water soluble solids, the total filtering area required to handle 180 tons of insoluble calcine leach residue per 24 hours will be given by:-

$$A = \frac{2240 \times 180}{0.75 \times 0.837 \times 20 \times 24} \text{ sq. ft.}$$

$$= 1340 \text{ sq. ft.}$$

In filtering this type of material the cloth blinding action will be fairly severe, and to give a filtering area comparable to that required under large scale operating conditions, the above figure would need to be divided by a factor of 0.7.

The filtering area required would therefore be of the order of 1900 sq. ft.

Assuming a similar area required at the second filtration stage, it would appear that, to handle the calcine residue by double filtration, would necessitate the installation of, say, three 14' x 14' drum filters, each with a filtering area of 616 sq. ft., at each of the filtration stages. These could possibly be replaced by two 14' x 24' units at each stage, giving a total filtering area of 3520 sq. ft.

The unfavourable filtering characteristics of the ground calcine led to consideration being given to the possibilities of handling the unground material by filtration.

To filter this type of material in practice, a top-feed unit, or one of the Dorcco type, would be essential. Top-feed filters, though designed primarily to handle rapid settling crystalline solids to give a dry but incompletely washed product, have also been adapted in a lesser degree to filter pulps containing insoluble solids. Barnebl [62] describes the dewatering and drying of minus 12 mesh foundry sands using one of these machines of the Swenson type. The capacity of this type of filter is given by Irvin [63] as between 5 and 35 tons per sq. ft. per 24 hours, depending on the nature of the feed and the amount of drying required. Thus even at the lower figure a 6 ft. x 6 ft. unit would handle 560 tons per day. Modern top-feed filters are fitted with a feeding device which not only distributes a coarse feed uniformly over the cloth but also removes undesirable fines from the feed by a form of hydraulic classification.

The Dorcco type of filter, as far as is known to the writer, is not in operation in this country but apparently finds a fairly wide application overseas. In this machine the filter medium is on the inside of the drum, while the pulp is fed into the bottom of the drum, thus eliminating the usual filter tank and agitator. The rapidity with which the solids settle helps considerably in forming a cake of uniform thickness and porosity which, when formed, is discharged at the top by means of a reverse air blow into a discharge chute. It is the type of machine suggested by Barnebl [64] as being suitable for handling a granular material where dewatering and washing are the important factors.

To duplicate strictly in the laboratory the conditions applying during the handling of 10 mesh alunite by machines of the types described above, special equipment would be required, but a reasonable approach to such conditions should be obtained by filtration in the ordinary Buchner filter funnel.

Information calculated to assist in assessing the possibilities of this type of filtration would include the determination of the percentage of water remaining in the filter cake when unground calcine was filtered, together with the percentage of water soluble salts left in the filter cake after filtration

- (a) without washing
- (b) after washing with a quantity of hot water equal to the moisture left in the cake.

A number of tests were accordingly carried out to obtain this information. In each test, calcine was extracted at 100°C. for 10 minutes, at a pulp ratio of 1 calcine to 1.5 water (except in Filter Test 81). The actual filtration took place at approximately 70°C.

By cake forming period is meant the time elapsed from transferring the pulp to the filter funnel until the level of the solution falls below that of the cake. Similarly the washing period is the time taken by the wash water to fall to the same level.

Five tests were made, using calcine obtained from an hour roast of -10+20 mesh material at a maximum temperature of 750°C. (Calcination Test 12).

The constant conditions during the tests were as follows:-

Vacuum	26 inches
Filter medium	No.5 Whatman paper.
Temperature of filtration	70°C. approx.
Pulp ratio	1.5 to 1
	1.9 to 1 (Test 81 only)
Draining time	60 seconds
Filter area	17.5 sq. inches.

The results are set out below in Table 31:-

Table 31. Filtration of Unground Calcine.

Filter Test No.	P u l p		Filter cycle - sec.		Wash water gm.	Filtrate (+ wash) c.c.
	Calcine gm.	Water gm.	Forming	Washing		
79	100	150	180	-	-	95
80	74	111	70	-	-	70
81	64	121	60	-	-	92
82	74	111	60	-	-	73
83	74	111	50	30	40	118
84	74	111	55	50	40	116

Filter Test No.	F i l t e r C a k e					Soluble salts recovered %
	Thickness inch	Wet. wgt. gm.	Water gm.	Water %	Dry cake % insoluble	
79	0.5	145	59.0	40.7	9.55	63.0
80	0.4	100	36.5	36.5	8.73	65.6
81	0.3	83	29.5	35.6	6.96	73.9
82	0.4	102	38.5	37.3	8.75	64.1
83	0.4	98	37.5	38.3	4.47	83.3
84	0.4	99	39.0	39.4	3.67	86.4

The average figure for the moisture in the wet cakes obtained in Tests 80 and 82 was 37.5 gm. Tests 83 and 84 were conducted under conditions identical with those of Tests 80 and 82 except that this amount of water (actually 40 gm. was used) was

applied as a hot water wash. Such a wash resulted in increasing the average water soluble salt recovery from 64.8% to 84.8%.

(d) Second Thickener:

Overflow from this unit, together with the filtrate from the second filter would make up the solution fed to the ball mill with the calcine. The underflow, at say 40% solids, would be further dewatered by filtration.

(e) Second Rotary Filter:

Assuming a feed of 40% insoluble solids to this unit, the amount of K_2SO_4 in the feed would amount to 8.1 tons per day. (180 Tons insoluble, plus 15 tons K_2SO_4 and 125 tons water from the first filter cake are repulped with 375 tons additional water. This is thickened to $1\frac{1}{2}$ to 1, giving a thickener underflow carrying 180 tons of solution containing $15 \times 270/500 = 8.1$ tons K_2SO_4 .)

From the filter cake moisture figures obtained in Filter Tests Nos. 77 and 78, it is apparent that the unwashed cake from this filter would contain approximately 3.75 tons of K_2SO_4 .

The above filter tests further show that in a normal Oliver filter cycle, washing of this cake is very inefficient and that therefore only a slight reduction in the above daily loss of K_2SO_4 can be expected.

D. Leaching Alternative No. 4

Counter-current Percolation Leaching:

(a) General:

The results of tests described under Sections A, B and C above, strongly stress the desirability of designing a plant which will produce a minimum quantity of slimes to be handled either by settlement or filtration, or by a combination of both. In this respect, the second leaching alternative, namely, leaching by counter-current washing in a series of classifiers, seems the most likely of the three alternatives so far described to meet with commercial success. Even here, the handling of the classifier overflow might easily be a source of trouble.

It is evident that many of these potential troubles could be overcome should it prove practicable to leach the calcine by percolating suitable solutions through stationary calcine charges contained in vats.

Except for charging and discharging of the vats, the mechanical operations involved in such a method consist solely of pumping solution from one vat to another. Operating costs are therefore light, and capital expenditure very low.

From the foregoing tests, a number of positive calcine characteristics, as opposed to the essentially negative ones of poor settlement and filterability, have emerged which would favour the percolation method of treatment. Of these, the chief are -

- (i) rapidity of solution of water-soluble content;
- (ii) the absence of any appreciable breaking down of calcine particles during water treatment;
- (iii) the retaining of the free percolating properties of a calcine charge as a result of (ii) above.

As the success or otherwise of vat leaching depends to a large degree on the free percolating properties of the material when treated under plant scale conditions, a first essential is a determination of the behaviour of the material under comparable conditions. Further tests which are indicated include a study of the relative merits of treating a charge in a single vat by straight out percolation, or by circulating the extracting solution through the charge a number of times; the possibility of obtaining effluent solutions saturated at an elevated temperature, and the efficiency of extraction obtained by using a limited amount of water only.

Tests carried out to obtain the required information will now be described.

(b) Percolation through a Four-foot Column of Calcine:

In percolation leaching the limiting factor is the time which is required for leaching and washing solutions to pass through the mass of material being treated. The following experiments (Leaching Test No.19) were carried out to give limiting values of these times, so that some idea could be gained of the time required for a cycle, and of the size of the vats required to obtain a day's through put of calcined alunite.

A cylindrical vat 4 ft. deep and 9 inches in diameter was made from two 2-ft sections of sewer piping. These two pipes were placed with their flanged ends upwards, the lower end of the upper pipe resting on a narrow strip of soft rubber seated in the flange of the lower pipe. This join was made water-proof by filling the flange with molten sulphur. When this had cooled it served to cement the two pipes and to prevent any leakage at the join. The lower end of the column was covered with a rubber cap which fitted over the outside of the pipe. This cap was tightly fitted and was clamped with a metal strip. An outlet was run from the centre of this cap through a hole in the base board on which the vat stood, and away to the vessels used for collecting the effluent.

A wooden false bottom was placed directly above the rubber cap in the vat. This was just a circular disc of wood with numerous $1/8$ " holes in it, and with a slightly raised flange around the edge so that the disc was raised off the rubber bottom. The disc was covered with a $1/4$ " layer of glass wool. The column was then filled with calcined alunite from Calcination Test No. 26. 85 lb. (38.6 kg.) of calcine were required to form the column.

The material is so porous that to start a percolation leach it is necessary to fill the vat with liquor (or water) from below, otherwise the air would not be displaced and short-circuiting would occur. This filling of the vat was carried out by running water from a large 15 litre bottle into the bottom of the vat under a head of about 9 ft. at the commencement of filling, and 3 ft. at the end. The limiting factors were the head and the size of the tap on the bottle. To fill the vat so that free water just appeared on the top of the vat required 11 minutes and the amount of water required was 32.2 litres.

The actual percolation test was carried out by keeping the top of the alunite covered with water at all times and allowing the effluent to run away through the bottom outlet as fast as this outlet would allow, or as fast as the effluent percolated, whichever was the faster. From the rates obtained it seems fairly certain that the former was the limiting factor.

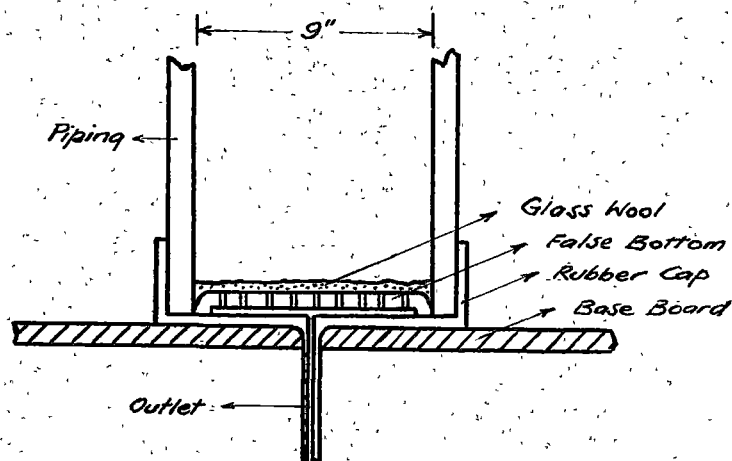


FIGURE XIII. PERCOLATION THROUGH 4 FT. COLUMN - VAT DETAILS.

As the rate was so fast, no further determinations with a larger outlet were considered necessary. The effluent was allowed to run out into 15 litre bottles and the times for running of each 15 litres were determined.

Preliminary laboratory scale experiments had shown that in each of the leaching stages of a leaching cycle, the amount of solution to be passed through the calcine was approximately 3 times the weight of the calcine being treated. As a limiting case, therefore, water equivalent to 3 times the weight of calcine was passed through the column. Cold water was used as it is more easily handled and the rate obtained would not be faster than that obtained using hot solutions. Thus the time was determined for 120 litres of effluent (= app. 3×38.6 kg.) to pass out of the column. In practice this quantity would include the amount draining out after displacement was stopped, but this amount was not known at this stage. It was determined later to be about 12 or 13 litres in from 15 to 30 minutes. Results are shown in the following table (Table 32).

Table 32. Percolation through Four foot Column of Calcine. (Leaching Test No.19)

<u>Filling of column:</u>		
Calcine required		38.6 kg. 85 lb.
Water required		32.2 litres 7.1 gallons
<u>Displacement percolation:</u>		
<u>Time</u>		<u>Effluent Volume</u>
min.	sec.	litres
-	-	-
2	10	15
4	20	30
6	25	45
8	35	60
10	45	75
12	55	90
15	5	105
17	20	120 *
19	30	135
* Thus: Average rate of percolation = 6.9 litres per min.		
= 1.5 gallons " "		
= 6.6 inches " "		

Draining:

Starting with free liquor just showing above the calcine:-

<u>Effluent volume</u> <u>litres</u>	<u>Draining time</u> <u>min. sec.</u>	
-	-	-
5	0	45
6	0	56
7	1	8
8	1	22
9	1	46
10	3	20
11	6	25
12	14	45
12½	26	-
13	50	-
13½	75	-

The graph below (Figure XIV) indicates the variation in rate of draining with time.

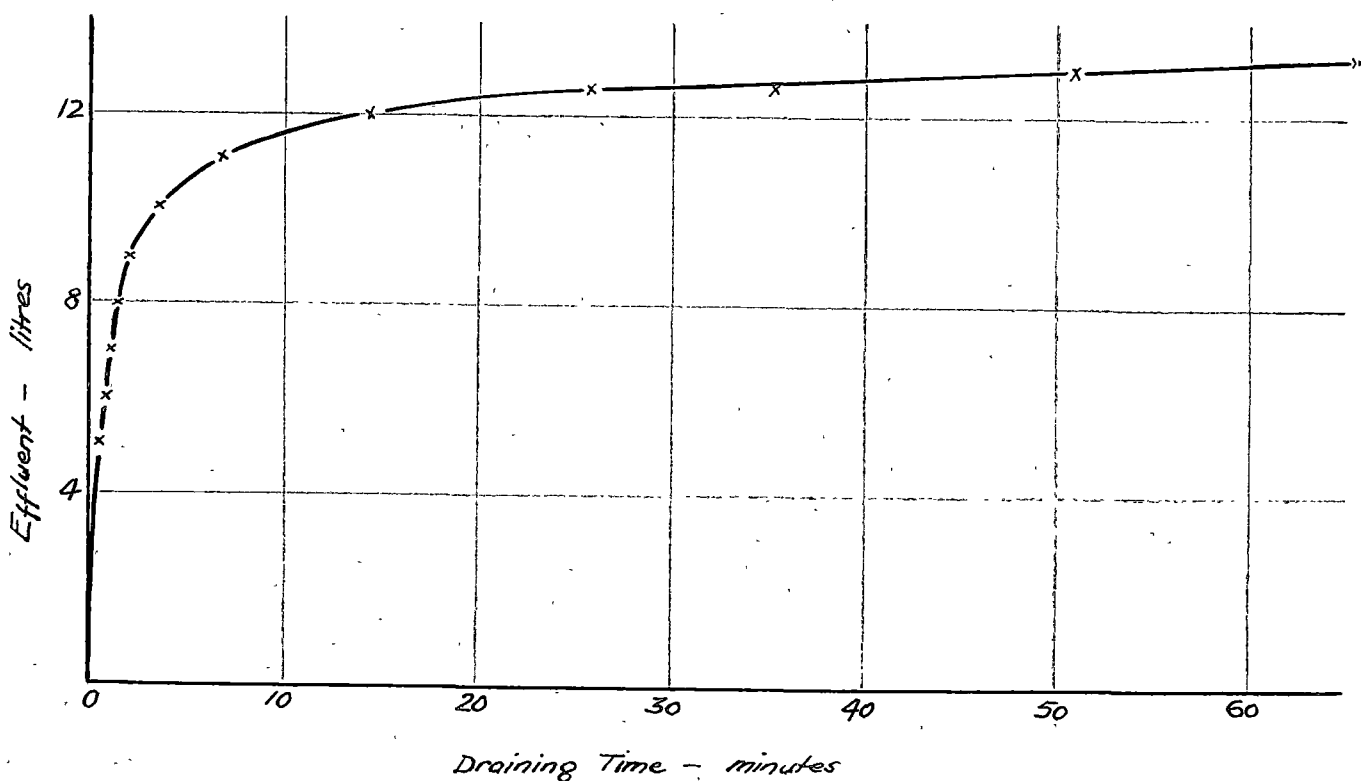


FIGURE XIV. RATE OF DRAINING OF CALCINE.

The results of the above test show that the rate of percolation of water through a four foot calcine charge is very satisfactory, indicating that even under the weight of the charge above, the lower layers of calcine retain their form and permeability during and after extraction of their water soluble salts.

(c) Nature of Solution Flow in Single Vat - Circulation v. Percolation:

Tests were conducted to determine the relative efficiencies of the following methods for the removal of the soluble salt content of calcine by vat leaching -

- (i) Allowing the extracting solution to percolate slowly once through the charge, the rate of addition of solution to the top of the vat to be the same as the rate of discharge from beneath the vat.
- (ii) Circulating the extracting solution continuously through the vat for a period of time sufficient to ensure the complete solution of all water soluble salts.

(i) The tests were made on 500 gm. charges of minus $\frac{1}{4}$ " calcine from Calcination Test No. 26. This calcine consisted of 22.7% water soluble salts, the test charges therefore containing 113.5 gm. of these salts.

The vat used was a tall 1 litre pyrex beaker, $3\frac{1}{2}$ " diameter and $7\frac{1}{2}$ " deep, giving a charge depth of approximately $4\frac{1}{2}$ ". The extracting solution was stored in a flask fitted with a condenser and maintained at a temperature approaching 100°C . by immersion in a water bath. The covered vat was similarly kept between 90°C . and 100°C . in a second water bath, and the extracting solution syphoned on to the vat until the surface of the charge was just covered. A second syphon, by means of which the pregnant solution was drawn off from the bottom of the vat upwards through a central tube, was then started, the rate of flow of the syphons being adjusted so that the whole of the solution is passed through the calcine in approximately 1 hour.

In one test (Leaching Test 20) water was used as the extracting medium, and in a second test (Test 21) an extracting solution carrying 9.8 gm. of salts per 100 gm. of water was used. This solution consisted of -

K_2SO_4	54.7 gm.
Na_2SO_4	34.6 gm.
MgSO_4	8.7 gm.
H_2O	1000 gm.

(ii) The maximum recovery of salts by continuous circulation of extracting solution through the vat was determined theoretically. The figures shown for extraction by this method are calculated assuming the charge drained to the same moisture content as that of the corresponding percolation test.

The constant conditions during the above tests were:-

Treatment time	60 minutes
Average temperature	$92\frac{1}{2}^{\circ}\text{C}$.
Salts in calcine charge	113.5 gm.
Water in each extracting solution	1000 gm.

The results are shown in Table 33. The figures for the maximum recovery of salts by continuous circulation, arrived at by calculation, are shown as tests 20(a) and 21(a).

Table 33. Calcine Leaching - Percolation v. Circulation.

Leaching Test No.	Salts in Extraction Solution gm.	Total Salts in System A gm.	Effluent			Residue		Extracting Efficiency $\frac{B}{A} \times 100$ %
			Total weight gm.	Salts B gm.	Water gm.	Water gm.	Salts A - B gm.	
20	0	113.5	759	102.4	656.6	310	11.1	90.2
20(a)	0	113.5	-	78.3	-	-	35.2	69.0
21	98	211.5	882	171.0	711.0	289	40.5	80.8
21(a)	98	211.5	-	150.4	-	-	61.1	71.2

These results emphasize the advantage of continuous percolation at a controlled rate as opposed to continuous circulation of extracting solution within a vat.

(d) Cyclic Percolation Tests:

A large number of preliminary percolation tests were carried out to obtain information relative to the moisture content of the leached residue, the nature of the effluent solutions, the approximate crystal yields to be expected and the relative merits of hot and cold extraction.

Using the data thus collected, a continuous counter-current percolation plant was designed for laboratory scale operation. A continuous test (Leaching Test 22) was then made over a period of 14 days, during which over fifty extraction cycles were completed. This test is described in detail in the following pages.

Leaching Test No. 22 -

- (1) General - p.79.
- (2) The nature of the Leaching Cycle - p.79
- (3) Equipment Used - p.80
- (4) Commencement of Cycle - p.81
- (5) Experimental Procedure - p.82
- (6) Results
 - (i) Crystal Yield. p.84
 - (ii) Mother Liquors. p.88
 - (iii) Residues - p.89
 - (iv) Washing Liquors - p.91
- (7) Miscellaneous Results
 - (i) Elevation of Boiling Point of Crystalliser Feed - p.92
 - (ii) Composition Crystalliser Feed - p.93
 - (iii) Min. Feed to Crystalliser - p.94

LEACHING TEST 22

1. GENERAL.

The calcine used throughout the leaching test was from Calcination Test 26. In this calcination test, ungraded $\frac{1}{4}$ inch alunite was roasted at a maximum temperature of 750°C . The material was fed to the furnace at the rate of 1 cwt. per hour and remained under treatment for 40 minutes.

A grading analysis of the resulting calcine gave the following figures:-

<u>Mesh</u>	<u>Aperture (inches)</u>	<u>Weight (%)</u>
-1/4"+1/8"	1/8	43.3
-1/8"+ 20	1/40	33.9
- 20 + 40	1/80	13.1
- 40 + 60	1/120	4.1
- 60 + 80	1/160	0.4
- 80 +100	1/200	2.8
-100 +200	1/400	1.8
-200	-	0.6

On extraction by agitation with an excess of hot water, 22.7% of the calcine was recoverable as water soluble salts. Of these salts 54.9% consisted of K_2SO_4 (representing a 75% recovery of potash), the remainder being chiefly sodium and magnesium sulphates in the approximate ratio of 3 Na_2SO_4 to 1 MgSO_4 , while small quantities of calcium and aluminium sulphates were also present.

2. THE NATURE OF THE LEACHING CYCLE.

The object of the crystallizing cycle was to prepare a saturated solution at an elevated temperature, cool the solution to some lower temperature, depositing the crystalline product, then to use the filtered mother liquor as part of the next leaching solution with which once again to prepare a saturated solution at the same elevated temperature.

In the case of the mixture in use here of sodium and potassium sulphates (together with smaller amounts of magnesium and calcium sulphates), glaserite ($3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$) is the crystalline type to separate in the early cycles. This is rich in potassium sulphate, and consequently leaves a solution rich in sodium sulphate. This can obviously only occur a limited number of times before phase rule considerations prevent the crystallization of a pure glaserite, and sodium sulphate or some other crystal product also begins to separate out on cooling the pregnant solution.

The purpose of this work was to find how many cycles could be run before this limiting stage was reached, and when reached to find what to do with the resulting solution.

Theoretical considerations decide to some extent the number of vats required to obtain complete extraction of all wanted salts from the calcined alunite. These can not take into account, however, the effect of the various salts present on the solubilities of the others. It is possible, however, to decide on an approximate minimum number of vats to be used.

The total number of vats decided upon was twelve. Of these nine were to be used for washing and three for extraction at elevated temperatures. The use of three extraction vats

requires that the sodium-rich mother liquor be returned to the cycle at the third vat, this procedure being adopted because it was estimated that at this point the total water soluble salt content of the washing solutions would, on an average, most closely approximate that of the mother liquor.

3. EQUIPMENT USED

The vats used in this test were specially constructed for the work. A vat consists of a vertical cylindrical copper vessel $5\frac{1}{2}$ inches deep by $3\frac{1}{2}$ inches in diameter. The top of the vat is open. The bottom consists of a shallow cone, pointing downwards, about $\frac{1}{2}$ " in height. The outlet from the vat is situated at the bottom of this conical depression and consists of a piece of $\frac{1}{4}$ " copper tubing, $1\frac{1}{2}$ inches long, soldered on to the vat. Next to the vat the outlet tube is surrounded by (and soldered to) a fitting for holding the vat in the water bath. This fitting consists of a brass piece about 1" in diameter by $\frac{3}{8}$ " long with a flat bottom to act as seat for a rubber washer. The lower part, about $\frac{1}{2}$ " in diameter by $\frac{3}{8}$ " long, is threaded. This threaded part is run through the bottom of the water bath. The whole joint is made watertight by screwing a nut onto this threaded part on the outside of the water bath.

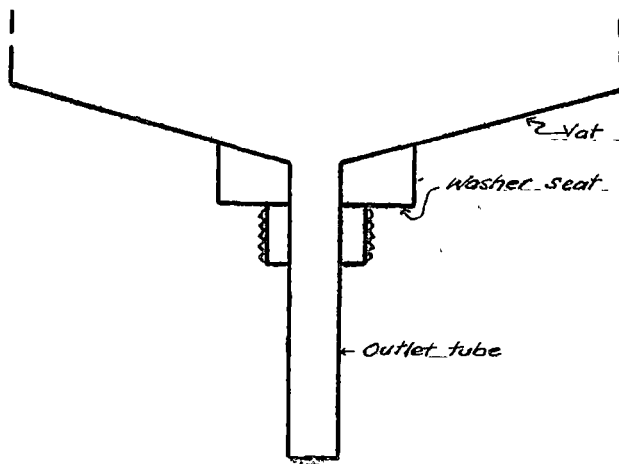


Figure XV. Vat Details

The vats are only used in combination with the water baths when they constitute part of the leaching series. In this case the vats are covered with slightly conical covers, the cone pointing downwards. These covers are necessary to minimise evaporation losses.

The waterbaths, only used in the leaching series, consist of vertical cylindrical copper vessels with flat bases and open at the top. There is a circular hole ($\frac{1}{2}$ " diameter) in the centre of the base to allow the outlet of the vat to pass through. The dimensions of the waterbaths ($6\frac{1}{2}$ " by $7\frac{1}{2}$ " diameter) are such that when a vat is in the waterbath there is an annular space 2" wide to hold the heating water. The conical shape of the bottom of the vats allows for water to also enter under the bottom of the vats to within $\frac{1}{2}$ inch of the centre. In this way it is possible to use a ring burner for heating the baths and in practice ring burners of $3\frac{1}{2}$ " diameter were used. There is an outlet tube at the bottom of the water bath at the side for emptying the bath before removing a vat to the washing series. Each bath is supported by means of three iron hooks let through the copper at the top of the bath. These hooks fit over the crosspieces of a tripod. The tripod was made so that the three vats in the washing series could be placed one above the other. By this arrangement it is possible to run the leaching solution by gravity through all of the leaching vats.

In the washing series the vats are cold and the waterbaths are not used. In this case the vats are stood in retort stands clamped to a vertical steel rod. All of the washing vats were placed in this vertical series, there being sufficient space between vats for manipulating a burette clip on a short piece of rubber tubing connected to the vat outlet. The rate of flow of the washing solution through the washing vats is regulated by adjusting these clips.

The vats are all fitted with false bottoms. A perforated porcelain disc 1" in diameter fits over the vat outlet inside the vat. A circular piece of hessian fits over the bottom of the vat and over this disc. The alunite is placed on top of this hessian. The charge used was, in every case, 500 gm. of dry roasted alunite.

4. COMMENCEMENT OF CYCLE.

Results from preliminary leaching tests have shown that a vat which has reached the stage where it is ready for dumping contains about 300 gms. of moisture in the residue.

In commencing this leaching test all of the vats used contained fresh calcine in both the washing and leaching series, there being 9 vats in the washing series and 3 vats in the leaching series. This means that in addition to the water required for the final effluent twelve lots of 300 gms. of water must be added to replace the moisture taken up by the vats. The effluent is required to consist of 1500 gms. of water plus the dissolved salts. This quantity is necessary so that in the temperature cycle between 30° and 90°C. the solution can take up the required amount of salts entering the cycle. This means that 5100 gms. of water must be added to the last washing vat (L), giving 4800 gms. of water (plus some dissolved salts) on to washing vat K. At the end of the washing series 2700 gms. of water (plus dissolved salts) passes on to washing vat D, and the effluent from D (2400 gms. of water, plus dissolved salts) constitutes the leaching solution for the leaching series. It has been found by experience that preparation of the leaching solution in this manner gives a solution near to saturation at room temperature. These figures for the quantities of water on to and off the vats in the washing series are arbitrary as no actual determinations were made of the quantities of these solutions involved. Determinations were made of the quantity and salt content of the effluent from washing vat D.

Water on to washing vat L	5100 gms.
Solution off washing vat D		
i.e. leaching solution	3085 gms.
Salt content	487 gms.
Water content	2598 gms.

This solution, prepared by leaching with cold water, was a pale golden colour and showed the presence of small quantities of aluminium. On heating to 97°C. prior to its use as extracting solution, an appreciable quantity of brown gelatinous sludge settled out. This was syphoned with the solution on to the hot vats, the effluent from which was quite clear and relatively free from aluminium. After the first cycle, no further coloured solutions were obtained.

The prepared leaching solution, when passed from the series of washing vats, all of which were cold, to the series of three leaching vats, in which solutions and solids were all kept above 90°C., was first heated in the apparatus previously described.

Each of these three leaching vats was dried in an air oven at 120°C. for several hours before being included in the circuit, and in all subsequent cycles the fresh vat brought in was subjected to the same treatment.

In passing through the three (fresh) leaching vats the solution loses (approximately) a further 900 gms. of water, so that the final pregnant solution will consist of about 1500 gm. of water together with a large quantity of dissolved salts.

Solution off leaching vat A was 2238 gms.

The pregnant solution was cooled to 30°C. with deposition of crystals (essentially glaserite at this stage). These crystals were filtered and dried.

Weight of dry crystals 102 gms.

Weight of mother liquor 2124 gms.

This yield of glaserite constituted the yield for the first cycle.

The final washing vat L was removed from the washing series, all of the vats being moved up one place (so that vat K of the first cycle now becomes vat L in the second cycle) and the last leaching vat (C) was added to the washing series, becoming washing vat D. A fresh leaching vat was introduced in the bottom of the leaching series as vat A of the second cycle.

The second cycle (and subsequent cycles) consisted of passing through the series of washing vats a quantity of water (and only that quantity) which would compensate for the water thrown out with the last washing vat when this was dumped. However, in addition to this, it was found necessary to add some water to compensate for evaporation losses. This also was added through the washing series and consisted on an average, of 150 gm. of water per cycle. This water passed through the washing series and, after proper time for draining, formed part of the leaching solution. The remainder of the leaching solution was made up of the mother liquor from the crystals in the previous cycle.

The following diagram (Figure XVI) illustrates the procedure schematically and includes the experimental figures for the first three cycles.

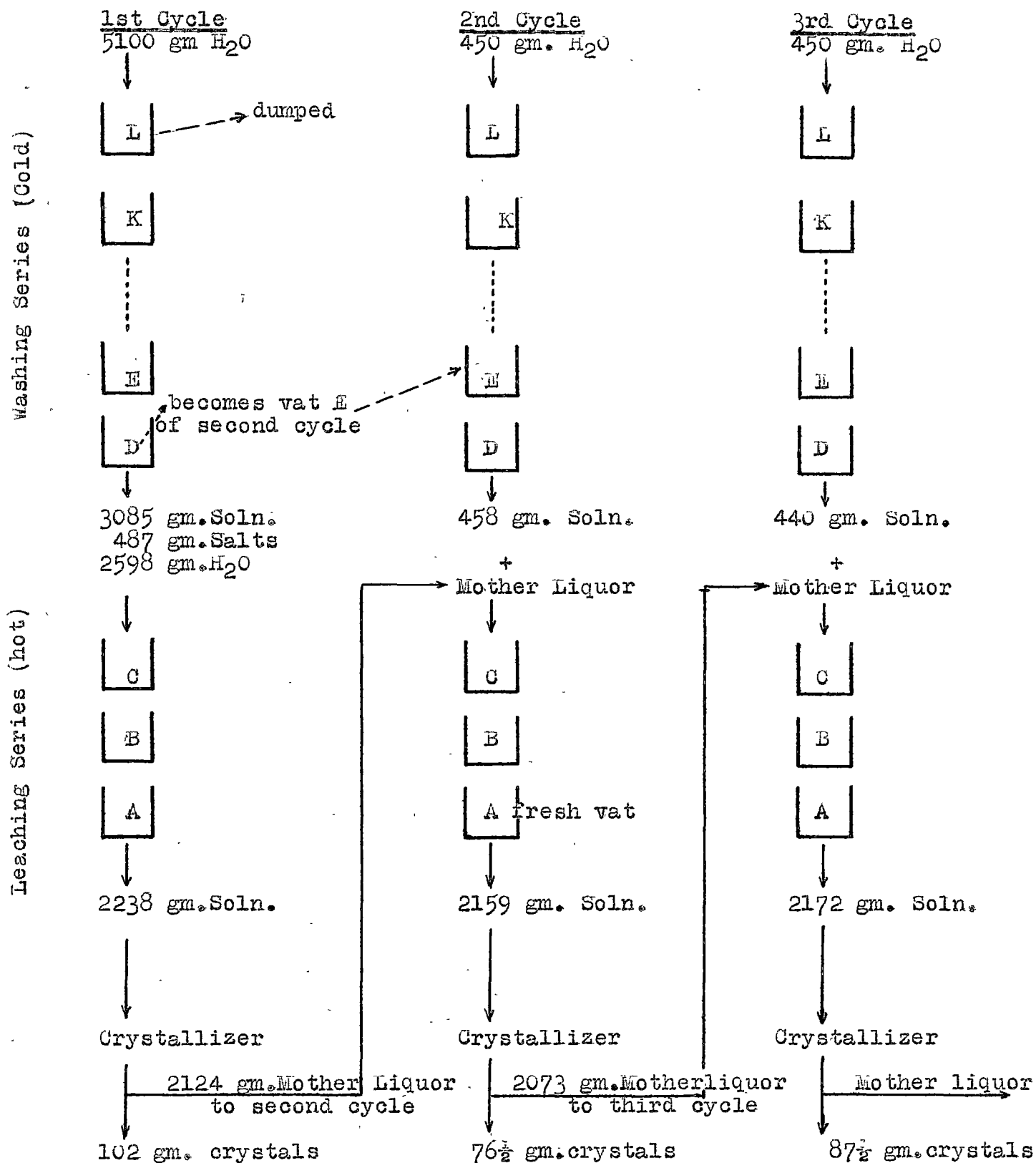
5. EXPERIMENTAL PROCEDURE.

The following notes give details of the various manipulations involved in the running of any one cycle.

The washing solution (water) to be added to the last washing vat was kept in a cylindrical funnel. The rate at which this solution flowed onto the vat was such that all of the washing solution passed through any vat in about 15 minutes.

In washing any one charge, the vat outlet was closed and wash solution run in until free liquid appeared above the charge surface. This took approximately five minutes. The outlet was then opened and the rate of flow adjusted so that inlet and outlet rates were identical. After an interval of about 5 minutes, the vat above will have drained fairly completely and the liquid on the vat being washed will therefore sink below the surface of the charge. In roughly 15 minutes from the time of commencement of the wash, the vat will have drained until the effluent is reduced to an occasional drip. A further period of 20 minutes draining was allowed before closing the outlet.

Figure XVI. Progressive Cycles, Leaching Test 22.



Vat L (at the top of the washing series) was then discharged and the residue weighed while wet and then again after drying at 120°C. for at least 8 hours.

The total residual salts in this residue were determined by heating the dried residue with a known excess of distilled water for 2 hours, and then determining the total dissolved solids in the resulting filtered extract. This quantity was determined for every fifth residue, while a total analysis of the residual salts was made on every tenth residue.

The effluent from the last washing vat (D) was mixed with the leaching solution for the current cycle. This solution was heated in a round bottomed flask immersed in a water bath. The solution was run out of this flask at about 97°C. on to the top leaching vat by means of a rubber syphon tube with a burette clip for regulating the rate of flow. The outlet from each leaching vat is fitted in the same way with a burette clip for regulating the rate of flow.

Much the same rate of flow was used in the leaching vats as in the washing vats, but here the larger bulk of solution made the time of passage through a vat considerably longer, usually of the order of 60 minutes.

As before, the outlet of a vat was not opened until sufficient solution had been added from the vat above to show free liquor on the charge surface, at which stage inlet and outlet rates were adjusted to keep the surface of each charge just covered with solution. From the time liquid first appeared on the surface until the whole of the extracting solution had been added to the vat a period of about 60 minutes had elapsed. A further draining time of 15 minutes was allowed for each of these hot vats.

From the foregoing it will be seen that a fresh vat entering the circuit will be in contact with hot extracting solution for 60 minutes in each of the positions A, B, C in the leaching series; it will have a further contact with wash solutions of, say, 15 minutes in each of the washing positions from D to L. Thus the total treatment time of any one charge was 3 hours extraction and 2½ hours washing - an overall period of 5½ hours.

The effluent from vat A was run into a 2-litre flask fitted with a condenser to prevent loss of moisture by evaporation of the hot liquors.

This pregnant solution was weighed and then cooled gradually to 30°C., the cooling taking at least one hour to complete. The resulting crystals were filtered rapidly on a Buchner funnel and allowed to drain in the funnel under full vacuum for 15 minutes. The wet crystals were then weighed, dried overnight at 120°C. and reweighed.

The mother liquor (filtrate) was weighed and returned with the effluent from the washing series to the extraction solution flask.

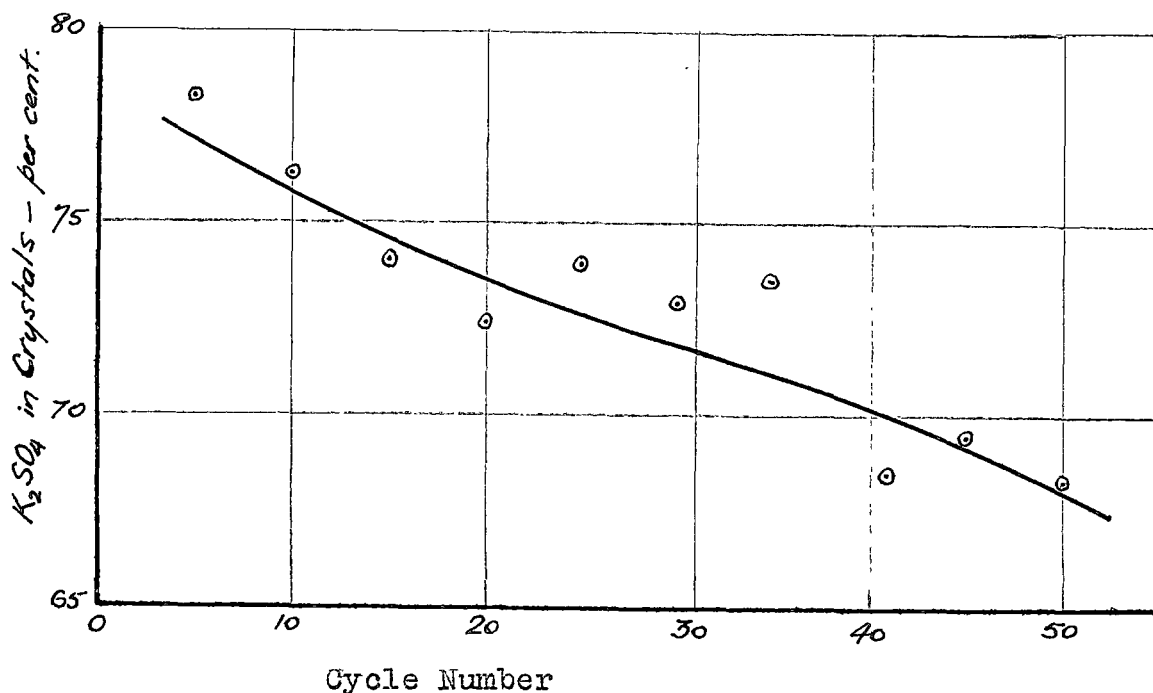
The mother liquor was sampled at every fifth cycle for determination of total dissolved solids and at every tenth cycle for a complete analysis.

6. RESULTS.

(a) Crystal Yield.

The yield of crystals obtained from successive cycles showed no regular trend, and was reasonably constant in the region of 90 grams (dry weight), with a maximum variation in either direction of about 10 grams.

Figure XVll: K₂SO₄ content of crystals.



The potassium sulphate content of the crystal yields was determined, and it showed a steady decrease as the number of cycles increased. The first crystals obtained contained 78.3 per cent K₂SO₄ and the crystals from cycle 50 contained 68.3 per cent K₂SO₄. The graph above (Figure XVll) shows the variation of the K₂SO₄ content of the crystals as the leaching test proceeded. The K₂SO₄ in the crystals (percent) is plotted for every fifth cycle with the exception of cycle 40, where cycle 41 is substituted.

The moisture content of a wet crystal yield depends of course, largely on the method of draining; but with a standard draining procedure and with constant yields of crystals it was expected that the moisture would also be constant. This, however, was found not to be the case. The moisture content showed a definite increase as the number of cycles increased. This was very probably due to the formation of hydrated double salts with magnesium. This agreed with the increase in the magnesium content of the crystals as the test proceeded.

Figure XVlll: Moisture in Crystals after Standard Draining.

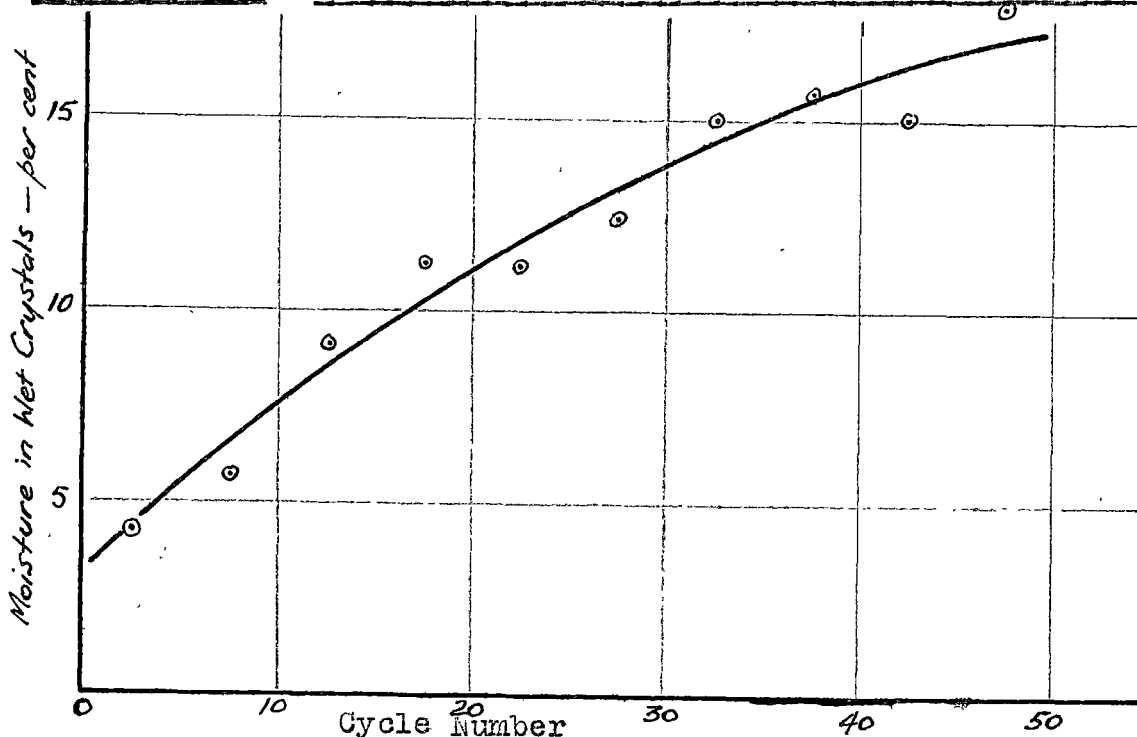


Figure XVlll represents the graph of the average moisture content of each five cycles against the number of the cycle. The moisture is expressed as the percentage of the moist crystal weight.

As the leaching test proceeds the various solutions become progressively more and more concentrated with respect to the total salts dissolved. This could be due to the fact that the concentrations of sodium and magnesium sulphates, relative to potassium sulphate, are increasing. As each of these salts is more soluble than potassium sulphate, the total amount of salts that the solution can hold will increase. The decrease in purity of the salt formed is due partly to the salts contained in the amount of mother liquor left wetting the crystals; but the amount of this impurity was determined and it was not sufficient to explain the full decrease in the K_2SO_4 content of the crystals. There must have been other salts than glaserite crystallizing.

The table following (Table 34) shows various analyses of crystal products which were made throughout the test. The yield of crystals is given both wet, as taken off the filter, and dry. The moisture content is the difference between these two weights. Although the difference represents water, this water would in fact be a part of a mother liquor solution. This means that part of the dry crystal yield is due to evaporated mother liquor. By determination of the total salts dissolved in the mother liquors for various cycles, it is possible to calculate the amounts of salts introduced in this way. This has been done for every tenth cycle as shown in the table.

In practice it would be possible to wash the wet crystals with either water or a concentrated glaserite solution to remove the adhering mother liquor. As the mother liquor is largely responsible for the impurities in the crystals, this would raise the grade of the salts sufficiently to make them much more readily acceptable as a commercial product. Or, if a set minimum grade must be obtained, many more cycles can be run before the purity drops below this.

The analyses whereby the salt contents of the adhering mother liquors were determined will be shown later. Here, however, the results are used to show the grade of crystal product obtainable with washing. If the crystals were not washed, and assuming an arbitrary minimum permissible purity of 70% K_2SO_4 , about 40 cycles could be run before some alteration in process would have to be made. If the poorer crystals were mixed with the better ones, the average grade would be well above 70% (actually 72.8%) for at least 50 cycles. In the case of washed crystals the average grade would be about 75.3 per cent for the 50 cycles. Without mixing, the grade of washed crystals is well above 70% at the 50th cycle (73.1%).

Table 34. Crystal Yields, Leaching Test 22.

Cycle No.	Crystal Yield				A n a l y s e s				K ₂ SO ₄ i n			Washed Crystals gm.	Calculated analysis of crystals after washing			
	Wet gm.	Dry gm.	W a t e r		K ₂ SO ₄ %	MgSO ₄ %	CaSO ₄ %	Na ₂ SO ₄ *	Total yield gm.	m.l.with crystals gm.	washed crystals gm.		K ₂ SO ₄ %	MgSO ₄ %	CaSO ₄ %	Na ₂ SO ₄ *
			gm.	% of wet yield												
5	98	93	5	5.1	78.3	-	-	-	72.8	0.70	72.1	91.5	78.8	-	-	-
10	83	76	7	8.4	76.2	1.00	0.15	22.7	57.9	1.34	56.6	73.5	77.0	0.6	0.2	22.2
15	109	98	11	10.1	74.1	-	-	-	72.6	-	-	-	-	-	-	-
20	112½	99	13½	12.0	72.5	2.04	0.31	25.2	71.7	1.86	69.8	93.9	74.9	1.1	0.3	23.6
25	100	88½	11½	11.5	74.0	-	-	-	65.5	-	-	-	-	-	-	-
30	112	93	19	17.0	73.0	3.62	0.21	23.2	67.9	2.70	65.2	84.1	77.6	2.3	0.2	19.9
32	109	89½	19½	17.9	-	3.82	0.38	-	-	-	-	-	-	-	-	-
34	155	128	27	17.4	72.1	4.10	0.33	23.5	92.3	-	-	-	-	-	-	-
35	108	94	14	13.0	73.6	-	-	-	69.2	-	-	-	-	-	-	-
36	102½	83	19½	19.0	-	4.04	0.44	-	-	-	-	-	-	-	-	-
38	113	98	15	13.3	72.7	3.34	0.42	23.5	71.2	-	-	-	-	-	-	-
41	103½	84	19½	18.8	68.5	-	-	-	57.5	2.84	54.7	74.1	73.8	-	-	-
42	103	88½	14½	14.1	-	3.77	0.44	-	-	-	-	-	-	-	-	-
44	122	104	18	14.8	-	3.94	0.47	-	-	-	-	-	-	-	-	-
45	109½	94	15½	14.2	69.5	-	-	-	65.3	2.22	63.1	85.4	74.7	-	-	-
46	117	96½	20½	17.5	-	9.43	0.41	-	-	-	-	-	-	-	-	-
48	139	114½	24½	17.6	-	12.50	0.42	-	-	-	-	-	-	-	-	-
49	133	109	24	18.0	65.1	-	-	-	70.9	3.19	67.7	95.8	70.7	-	-	-
50	104	89	15	14.4	68.3	5.66	0.68	25.3	60.8	2.02	58.8	80.4	73.1	4.4	0.8	21.7
51	101	83½	17½	17.3	66.7	10.48	0.83	22.0	55.7	2.44	53.3	73.8	72.2	9.6	0.9	17.3

* By difference.

(b) Mother Liquors:

It has been stated above that the concentration of salts dissolved in the mother liquors increased as the test proceeded. This can readily be seen by reference to Table 35, below. The weight of mother liquor throughout the test was fairly constant as this was one of the conditions adhered to. The most interesting results of the analyses of the mother liquors are those represented by the $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4$ ratio. From a value of less than one in the early cycles this ratio rises to $2\frac{1}{2}$ to one in the later stages while fairly pure glaserite (78% K_2SO_4) is still crystallizing from the solutions.

Table 35. Mother Liquors, Leaching Test 22

Cycle No.	Weight of M.L. gm.	Dissolved Salts		Analyses of dissolved salts									
		gm.	gm/100 gm. %	Weight in Solution gm.					Na ₂ SO ₄ K ₂ SO ₄ Ratio	Percentage of total salts			
				K ₂ SO ₄	MgSO ₄	CaSO ₄	Na ₂ SO ₄			K ₂ SO ₄	MgSO ₄	CaSO ₄	Na ₂ SO ₄
5	2238	521	23.3	239.8	49.7	tr.	231.5	0.97	46.0	9.5	-	44.5	
10	2300	614	26.7	322.0	74.0	"	218.0	0.68	52.5	12.0	-	35.5	
15	2201	641	29.1										
20	2183	649	29.7	211.0	108.0	"	330.0	1.56	32.5	16.6	-	50.9	
25	2194	687	31.3										
30	2285	731	32.0	220.4	119.6	"	391.0	1.77	30.1	16.4	-	53.5	
35	2219	728	32.8										
41	2253	757	33.6	217.3	135.5	"	404.2	1.86	28.7	17.9	-	53.4	
45	2028	721	35.6	187.2	134.0	"	400.3	2.14	26.0	18.5	-	55.5	
49	1880	667	35.5	161.2	121.6	"	384.2	2.38	24.2	18.2	-	57.6	
50	1993	728	36.5	170.4	128.1	"	429.5	2.52	23.4	17.6	-	59.0	
51	2113	751	35.6	189.6	132.2	"	429.2	2.26	25.2	17.6	-	57.2	

Figure XIX is a graph of dissolved salts in the mother liquor (grms/100 grms) against cycle number, and Figure XX of $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4$ against cycle number.

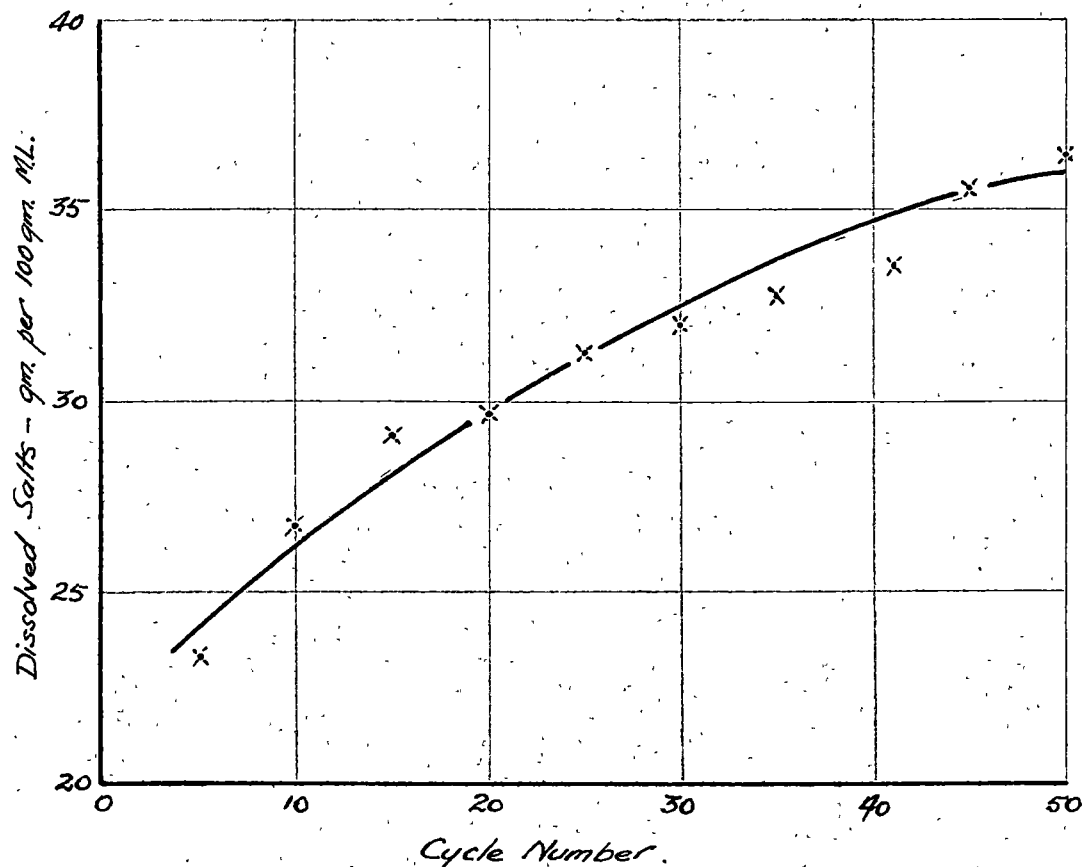


FIGURE XIX. SALTS IN MOTHER LIQUOR.

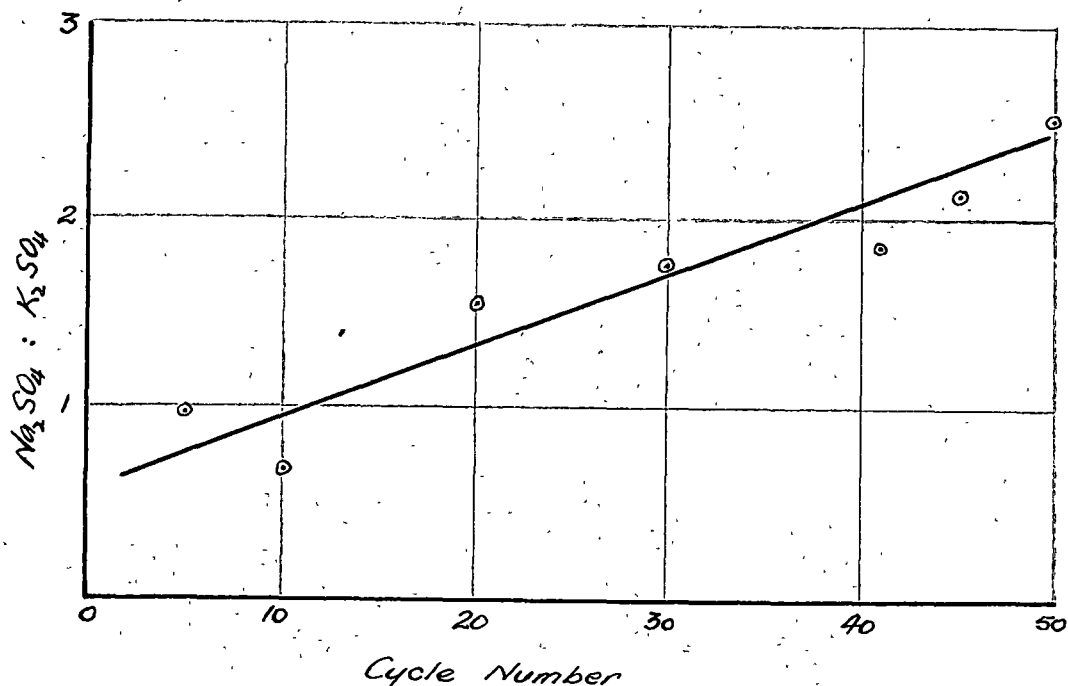


FIGURE XX. SODIUM - POTASSIUM RATIO IN MOTHER LIQUOR.

(c) Residues:

The insoluble or undissolved residues from vat L were dumped after each cycle. The weight of the dried residue was, on an average, just under 400 gms., indicating that over 100 gms. of the possible 112.5 gms. of water soluble salts had been recovered. The nature and quantity of the water soluble salts remaining in the calcine were determined by extracting the residue with a large excess of hot water. The residual water soluble salts were then determined by evaporating an aliquot of this extract to dryness. This was done for every fifth cycle and for every tenth cycle a determination was made of the nature of these soluble salts.

Table 36 (below) shows the results of these analyses. The weights of residual water soluble salts show a very marked decrease (see Figure XXI), which is very difficult to explain. This may be due simply to an approach towards an equilibrium. There was no variation in the method of washing. On the other hand it may be due to the fact that sodium and magnesium sulphates are building up in the solutions, and so in the vats, and these salts are more readily removed in the washing series.

It has been shown above that the Na₂SO₄/K₂SO₄ ratio in the mother liquors increased markedly with the increase of the number of cycles, changing from 0.7 at cycle 10 to 2.5 at cycle 50. In the case of the salts remaining in the residues a similar change occurs but not to anything like the same extent. In cycle 10 the ratio is 0.48 and in cycle 50 it is only 1.34. This is in agreement with the above statement that the sodium salts are more readily removed from the washing series. Some rise in this ratio must be expected, of course, because of the large increase in the sodium content of liquors entering the washing series with vat D from the leaching series.

Table 36. Residues, Leaching Test 22.

Cycle No.	Weight of Residue gm *	Residual Water-soluble salts		Analyses of residual w/s salts			
		Weight gm.	Percentage of Residue	Percentage of total residual salts.			
				K ₂ SO ₄	MgSO ₄	CaSO ₄	Na ₂ SO ₄
5	400	10.6	2.65				
10	400	8.9	2.22	53.1	3.5	17.7	25.7
15	399	8.2	2.06				
20	400	7.0	1.76	41.5	2.6	17.7	38.2
30	400	6.6	1.64	37.8	2.9	14.9	44.4
35	400	6.4	1.60				
40	398	6.5	1.62	39.9	4.6	15.9	39.6
45	399	6.0	1.51	37.5	n.d.	n.d.	n.d.
50	397	5.4	1.34	36.4	4.6	11.5	47.5

* The weights given here are only rough weights taken to give an easy check on whether any considerable change was occurring. The accurate residue weight is, for any cycle, 387.5 gm. + the weight of residual salts.

Table 37 (below) shows the percentage extraction for Leaching Test 22, as calculated from the salt content of the residues. From the figures for the individual cycles it is possible to calculate the average extraction for the whole test, but the separate figures are more significant because of the very marked increase in the extraction as the test proceeded.

Table 37. Residue Extracts and Total Extraction, Leaching Test 22.

Cycle No.	Extracting Water gm.	Salts/25 ml. of Extract gm.	Water/25 ml. of Extract gm.	Salts in Extract gm.	Residual Salts % of total	Extraction %
5	1058	.2506	24.75	10.7	9.5	90.5
10	1280	.1736	24.83	8.95	8.0	92.0
15	1174	.1749	24.83	8.28	7.4	92.6
20	1157	.1519	24.85	7.07	6.3	93.7
25	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
30	1152	.1424	24.86	6.60	5.9	94.1
35	1217	.1309	24.87	6.41	5.7	94.3
40	1231	.1307	24.87	6.48	5.8	94.2
45	1247	.1209	24.88	6.06	5.4	94.6
50	1279	.1042	24.90	5.35	4.8	95.2
Average Extraction						93.5%

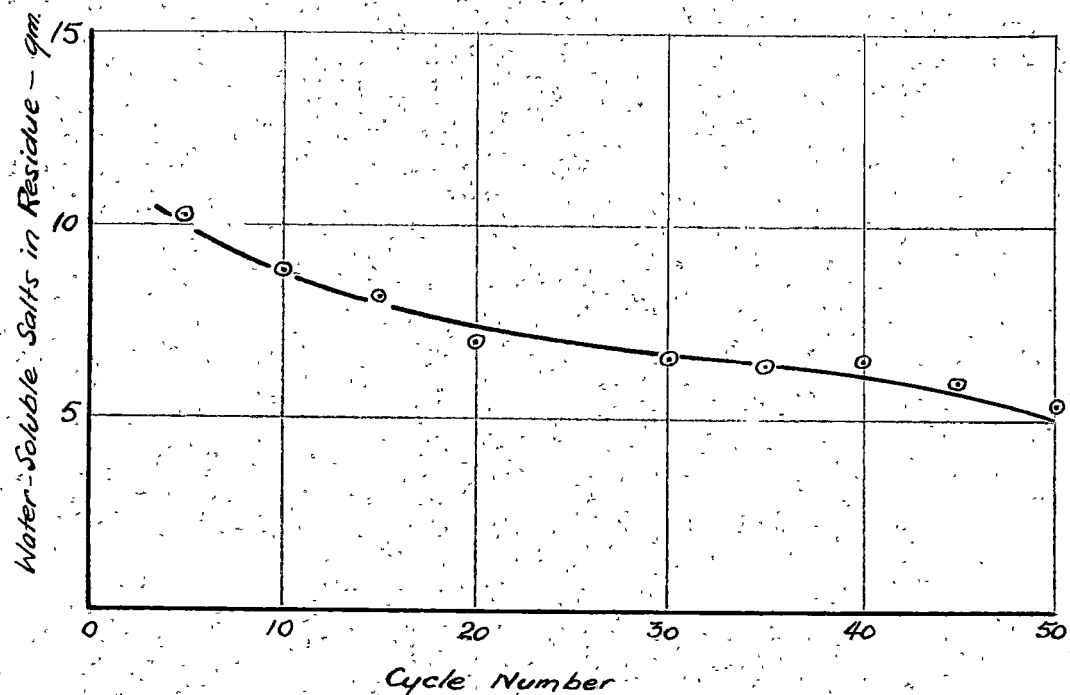


FIGURE XXI. WATER SOLUBLE SALTS IN RESIDUE.

(d) Washing Liquors:

Only two samples of the effluents from vat D of the washing series were taken. Table 38 shows the results of analysis of these solutions.

Table 38. Washing Series Effluents, Leaching Test 22.

Cycle No.	Weight of Effluent	Salts in Solution gm.	Salts in Solution %	Individual Salts - %			
				K ₂ SO ₄	Na ₂ SO ₄	MgSO ₄	CaSO ₄
40	486	121	25.0	7.15	13.4	4.3	.14
50	627	152	24.3	5.65	14.1	4.4	.22

It is interesting to note that the Na₂SO₄/K₂SO₄ ratios for these washing series effluents are practically identical with those of the mother liquors of the corresponding cycles, whereas the ratios for the residues have only half this value. (Table 39).

Table 39. Na₂SO₄/K₂SO₄ Ratios for Cycles 40 and 50.

Cycle No.	40	50
Na ₂ SO ₄ /K ₂ SO ₄ ratio in m.l.	1.86	2.52
" " wash	1.87	2.49
" " residue	.99	1.30

The low value of this ratio for the residues indicates that sodium salts are more readily removed in the washing series than potassium salts. The fact that the ratios are identical in the wash effluents and mother liquors shows that on this ground it is permissible to mix these two to give the leaching solution. However, reference to Table 35 (above) shows that the total salt concentration for cycles 40 and 50 are close to 35 per cent by weight. To mix the wash solutions, of roughly 25 per cent total salt concentration, with these solutions is inefficient. Changing the number of vats in the washing series could have some effect on these concentrations. However the minimum possible concentration of the mother liquor would be that of a solution (mother liquor) saturated at 30°C. The maximum concentration possible for the washing series effluent is that of a solution saturated at room temperature, as this is a cold washing series. Therefore it is not possible, with the maximum efficiency obtainable in both leaching and washing series to obtain two solutions - mother liquor and washing series effluent - which can be efficiently mixed. The only solution to this problem seems to lie in having the last stage (at the concentrated end) of the washing series carried out at an elevated temperature.

7. MISCELLANEOUS RESULTS

(a) Elevation of Boiling Point of Crystallizer Feed:

The mother liquor resulting from the crystallization stage of cycle 51 was diluted, heated to 100°C., and the original crystal yield added to the mother liquor. When solution was complete, the liquor was evaporated down until the salt concentration was the same as in pregnant solution 51, namely 37.8 grams of salts per 100 grams of solution.

The boiling points of this solution were determined at three arbitrarily chosen pressures, 760 m.m., 62.8 m.m. and 29.5 m.m. The boiling points of distilled water were measured at the same pressures and in the same apparatus.

The experiments were conducted in a flask fitted with a condenser, and, in the case of the two lower pressures, connected through the condenser to a vacuum pump.

The results are shown in the following table (Table 40) and are plotted on the attached graph (Fig. XXII). From the graph, the approximate boiling point elevations at intermediate pressures may be obtained by interpolation.

Table 40. Boiling Point Elevation of Crystallizer Feed.

Pressure m.m.	B.P. of solution °C.	B.P. of water °C.	B.P. elevation °C.	B.P. of water * °C.
760	103.8	100.2	3.6	100.0
62.8	47.7	43.4	4.3	42.4
29.5	35.2	29.8	5.4	28.7

* True b.p. figures for the corresponding pressures
(Handbook of Chemistry & Physics p. 1264).

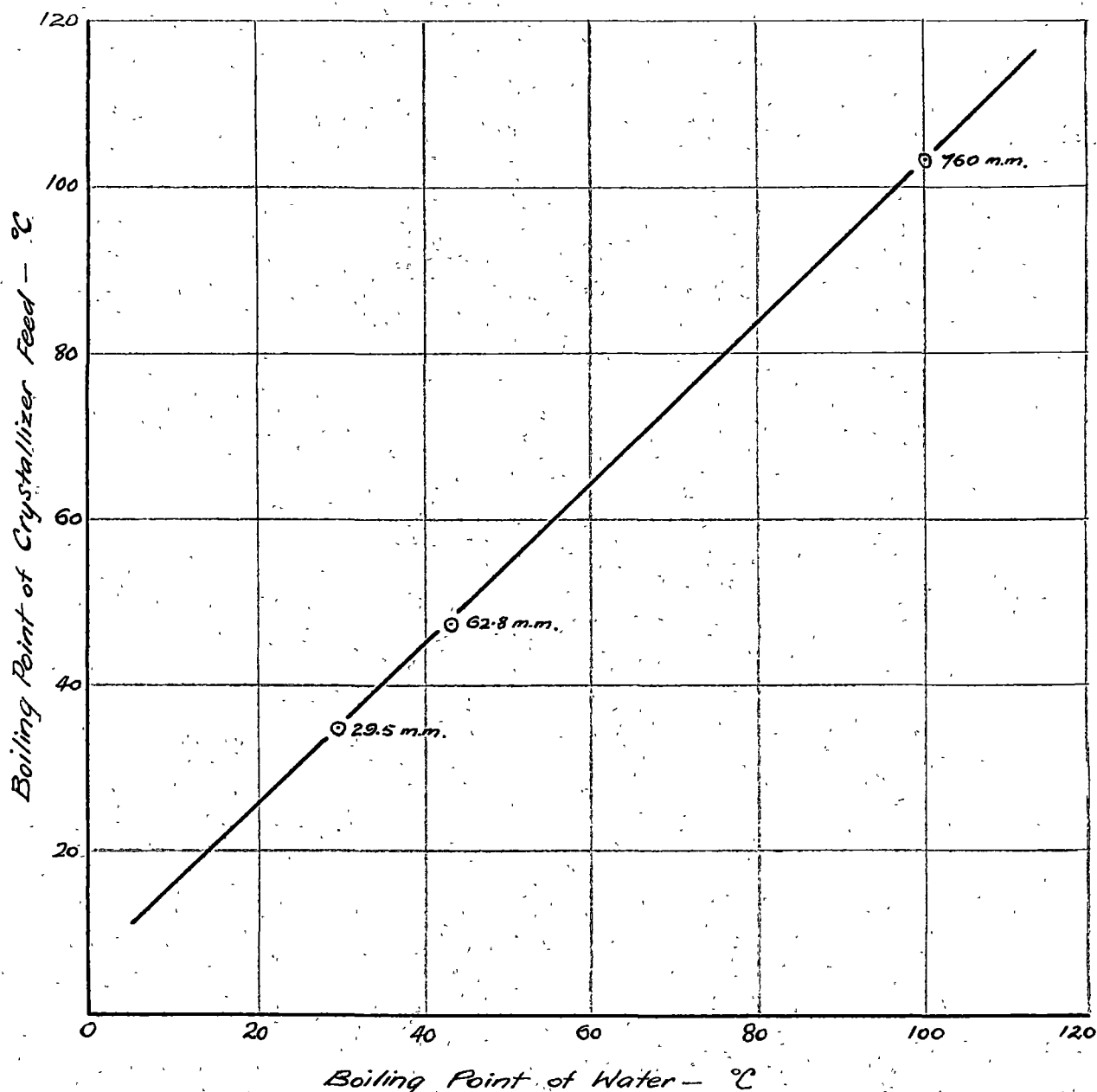


FIGURE XXII. BOILING POINT OF CRYSTALLIZER FEED.

(b) Composition of Crystallizer Feed:

Complete analyses of soluble salts in mother liquors were carried out only in Cycle Nos. 5, 10, 20, 30, 41, 45, 49, 50 and 51.

The following figures (Table 41) refer to cycles 20, 30, 41 and 51, and give the calculated compositions of the pregnant solutions with, for comparison, the compositions of the corresponding mother liquors.

Table 41. Composition of Crystallizer Feed.

Cycle No.		20	30	41	51
Dry weight of calcine charge	gm.	500	500	500	500
Extracting Solution	gm.	2683	2754	2784	2611
Pregnant Solution	gm.	2295	2400	2359	2217
K ₂ SO ₄	gm./100 gm.	12.3	11.8	11.6	11.2
MgSO ₄	"	4.8	5.1	5.9	6.4
Na ₂ SO ₄	"	15.5	17.5	18.2	20.4
CaSO ₄	"	trace	trace	trace	trace
Total Salts	"	32.6	34.4	35.7	38.0
Mother Liquor	gm.	2183	2285	2253	2113
K ₂ SO ₄	gm./100 gm.	9.7	9.6	9.6	9.0
MgSO ₄	"	4.9	5.3	6.0	6.3
Na ₂ SO ₄	"	15.1	17.1	18.0	20.3
CaSO ₄	"	trace	trace	trace	trace
Total Salts	"	29.7	32.0	33.6	35.6
Crystal Yield	gm.	99	93	84	83½

(c) Minimum Feed to Crystallizers:

In three leaching tests carried out (Nos. P₅, P₆, 22) the numbers of cycles completed were respectively 5, 17 and 51. In each case the calcine charge was 500 grams dry weight: in Test P₅ calcine from Calcination Test 21 (B) was used, this being a -10+20 mesh product carrying 20.2% of water-soluble salts. In Tests P₆ and 22, the calcine was the minus ¼ inch product from Calcination Test 26 (B), carrying 22.5% of water-soluble salts. P₅ and P₆ were two preliminary tests not recorded here in detail.

Results, together with some conditions under which these tests were carried out, are tabulated below (Table 42).

Table 42.

Test Number	5	6	8
Cycles completed	5	17	51
Average weight of pregnant solution	0.57	2.24	4.55
Charge weight			
Total crystal yield gm.	110	1197	4676
Average crystal yield per cycle-gm.	22	70.5	91.7
Total possible crystal yield per cycle - gm.	101	112.5	112.5
Average crystal yield	0.22	0.63	0.82
Possible crystal yield			

Table 42 (Continued):

Average K ₂ SO ₄ content of crystals - per cent.	75	74.7	72.8
Average yield of K ₂ SO ₄ per cycle-gm.	16.5	52.7	66.7
Total possible K ₂ SO ₄ yield per cycle - gm.	59.7	62	62
Average K ₂ SO ₄ yield	0.28	0.85	1.08
Possible K ₂ SO ₄ yield			

The average ratios of pregnant solution to dry weight of calcine charge were respectively 0.57, 2.24 and 4.55. The graph drawn below (Figure XXIII) shows these ratios plotted against the ratios -

(A) $\frac{\text{Average crystal yield}}{\text{Possible crystal yield}}$ and (B) $\frac{\text{Average K}_2\text{SO}_4 \text{ yield}}{\text{Possible K}_2\text{SO}_4 \text{ yield}}$

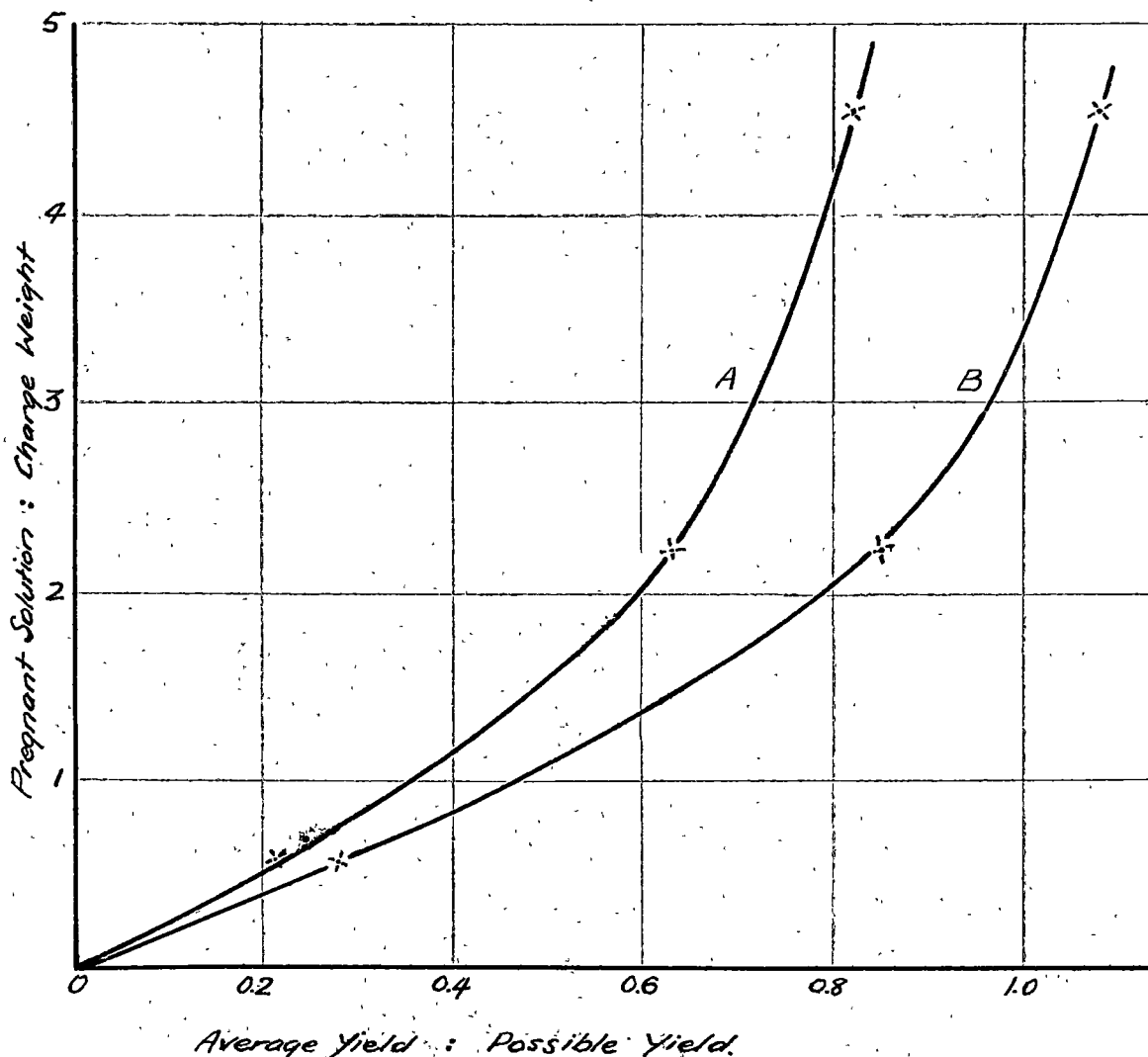


FIGURE XXIII. RELATIONSHIP BETWEEN SOLUTION - SOLID RATIO AND CRYSTAL YIELD.

The graph shows that the ratio (B) reached a value of unity when the ratio $\frac{\text{pregnant solution}}{\text{calcine charge}}$ was 3.4 to 1.

This ratio represents the minimum quantity of circulating solution necessary to obtain complete extraction of the potash salts. From this value of the ratio the minimum quantity of circulating solution required to give complete extraction of potash salts from any charge can be calculated.

The fact that the ratio (B) $\frac{(\text{Average } K_2SO_4 \text{ yield})}{(\text{Possible } K_2SO_4 \text{ yield})}$ reached a value greater than unity has been assumed to be an indication that the minimum value of the ratio $\frac{\text{pregnant solution}}{\text{calcine charge}}$ has been exceeded. The calculation of the required minimum quantity is based on this assumption. It is possible however for the minimum not to have been reached and yet for the above ratio (B) to exceed unity.

In the early cycles of a leaching test the K/Na ratio in both solutions and residues is very much higher than in the later stages. Therefore a larger quantity of circulating solution will be necessary in the later cycles, and the calculation of the necessary minimum ratio depends on the number of cycles to be run.

VII. SUMMARY AND CONCLUSIONS

The following paragraphs summarise the results of the test work detailed in the foregoing sections:-

1. The Lake Campion ore deposit covers an area of over 400 acres and is estimated to contain over 9 million cubic yards of alunitic material, averaging over 60% alunite.

140 acres were sampled to a depth of 3' 6" by the writer, revealing 1,200,000 tons of ore averaging 64.6% potash alunite or 13.7% K_2SO_4 . This alone represents Australian requirements of potash for 15 years at the present rate of consumption. It further represents 290,000 tons of alumina.

The solid gangue is mainly siliceous, SiO_2 averaging 21% throughout the tonnage sampled.

2. The subsurface water is acid and highly saline. As a result, the ore contains about 5% of water soluble salts, mainly as chloride and sulphate of sodium and magnesium, with traces of aluminium, calcium and potash. After calcination and extraction, these salts represent roughly half the recovery of water soluble salts.

3. Due mainly to the poor settling and filtering properties of the ore when pulped with water, the removal of these sodium and magnesium salts prior to calcination, does not appear to be a practical proposition. Washing of the raw ore by filtering and by counter current washing in thickeners has been shown to require prohibitively large filtering and settling areas.

4. Calcinations at maximum temperatures varying between $600^{\circ}C$. and $900^{\circ}C$. have been carried out in a pilot plant rotary kiln, 12 feet long by 16 inches internal diameter. The most favourable temperatures were found to be between $750^{\circ}C$. and $800^{\circ}C$., under which conditions a calcine is obtained containing 20-25% water soluble salts.

5. The material fed to the kiln need not be ground finer than minus $\frac{1}{4}$ inch to give a satisfactory calcine. The calcine so obtained retains its shape and mechanical strength after extraction with hot water.

6. From the flue gases, both HCl and H_2SO_4 may be recovered for subsequent use in the acid extraction of the potash residues for the recovery of alumina.

7. Four leaching alternatives are described and detailed experiments were carried out to test the feasibility of each. These tests stressed the necessity for designing a plant which would produce a minimum quantity of fines during extraction of the calcine. Like the raw ore, these fines were found to be very difficult to settle and to filter.

8. The extraction method shown to be most satisfactory consists in counter-current leaching of the calcine in vats by percolation with a series of solutions of decreasing concentration. By this means advantage is taken of the remarkably free percolating properties of the calcine carrying the normal amount of fines and the rapid solubility of the potassium sulphate (and other water soluble salts) in the leaching solutions.

9. By percolation leaching at an elevated temperature, a yield of glaserite ($3K_2SO_4 \cdot Na_2SO_4$) is obtained from the

leach liquors simply by cooling, thereby obviating the necessity for costly evaporators. The sodium- and magnesium-rich mother liquors are returned to the leaching circuit making the process cyclic and continuous.

10. The treatment method recommended consists then, of calcining minus $\frac{1}{4}$ inch air-dried ore at maximum temperatures between 750° and 800°C. , hot leaching the calcine by a cyclic counter-current percolation process, and recovering glaserite ($79\% \text{K}_2\text{SO}_4$) by cooling the effluent solutions, the mother liquors to be returned to the leaching system.

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