ATLANTIC ANALYTICAL SERVICES LIMITED
ANALYSTS & CHEMICAL CONSULTANTS
275 CITY ROAD, SAINT JOHN, NEW BRUNSWICK
E2L 3N3
TELEPHONE (506) 642-1117

SULPHUR DIOXIDE, ACETONE, WATER IN THE PREPARATION OF FERTILIZERS AND POTASSIUM CHEMICALS

PREPARED FOR:

DEPARTMENT OF REGIONAL INDUSTRIAL EXPANSION

BY:

W. J. WILSON
ATLANTIC ANALYTICAL SERVICES LIMITED
SAINT JOHN, NEW BRUNSWICK

MAY, 1984
CONTRACT # 3124

ATLANTIC ANALYTICAL SERVICES LIMITED
ANALYSTS & CHEMICAL CONSULTANTS
275 CITY ROAD, SAINT JOHN, NEW BRUNSWICK
E2L 3N3
TELEPHONE (506) 642-1117

SULPHUR DIOXIDE, ACETONE, WATER IN THE PREPARATION OF FERTILIZERS AND POTASSIUM CHEMICALS

PREPARED FOR:

DEPARTMENT OF REGIONAL INDUSTRIAL EXPANSION

BY:

W. J. WILSON
ATLANTIC ANALYTICAL SERVICES LIMITED
SAINT JOHN, NEW BRUNSWICK

MAY, 1984
CONTRACT # 3124

TABLE OF CONTENTS

INTRODUCTION

THE PROCESSES

TABLE OF CONTENTS (Cont'd)

DISCUSSION

Selection of Processes:

EXECUTIVE SUMMARY

The problem of disposing of waste sulphur dioxide is most frequently solved by converting the gas to sulphuric acid for use in fertilizer production. This report discusses the direct use of sulphur dioxide, in combination with acetone and water, to achieve the same objective, obviating the necessity for a sulphuric acid plant.

Several methods for producing potassium sulphate, monopotassium phosphate, and other phosphatic fertilizers are examined, along with the TVA dicalcium phosphate process, based on the same chemicals, and the Israel Mining Industries process, based on waste hydrochloric acid. Schematic flowsheets, material and energy balances are presented for each process studied.

The preferred processes involve continuous countercurrent ion exchange and produce potassium bisulphite, potassium sulphite, potassium sulphate, monopotassium phosphate, and complex potassium phosphates without differentiation; technical, food, feed and fertilizer grade phosphoric acid in all marketable concentrations; hydrochloric acid, calcium chloride; and liquid sulphur dioxide.

It is demonstrated, also, that considerable production of sodium chemicals logically follows and that markets for them exist in Atlantic Canada and neighbouring parts of the U. S. A.

The estimated f.o.b. value of the production of potassium sulphate (50,000 tonnes/year), monopotassium phosphate (100,000 tonnes), and sodium chemicals (100,000 tonnes), is $48,000,000/year.

A significant additional advantage is that there is an excellent opportunity for design and construction engineers in New Brunswick to develop international markets for this technology, because small plants are entirely

feasible, which creates a new concept in fertilizer manufacture: local production to supply autonomous areas.

Recommendations include cost-benefit analysis of the processes, a small pilot plant, and funding for further bench-scale studies; also, that the risk to entrepreneurs embarking on the use of this technology be minimized by substantial government assistance to prototype plants.

A consistent, two-pronged approach is presented, to the manufacture of secondary products in the potash industry and to the utilization of waste sulphur dioxide, without the need for massive research or capital expenditures.

CONCLUSIONS

As a result of the work of this study, the following conclusions can be drawn:

1. The use of Pritchard-Fraxon solutions in the potassium, sodium, and phosphorus chemicals industry, including fertilizer manufacture, appears to be technically straightforward and energy efficient.

2. The preferred processes for making these chemicals involve continuous countercurrent ion exchange followed by product recovery.

3. The following products are possible with this technology:

    a. potassium bisulphite, potassium sulphite, potassium sulphate, monopotassium phosphate, and complex potassium phosphates without differentiation.

    b. a similar series of sodium compounds.

    c. technical, food, feed, and fertilizer grade phosphoric acid in all marketable concentrations.

    d. other important industrial chemicals, such as hydrochloric acid, calcium chloride, and liquid SO_2.

Note: Assuming production of 50,000 tonnes/year of K_2SO_4, 100,000 tonnes of monopotassium phosphate, and 100,000 tonnes of sodium chemicals for the pulp and paper industry in the Maritimes, Maine, and the Gaspé/year;

using the realizable prices used in the Kilborn study, and conservatively estimating sodium chemical prices at the price of saltcake, which is the cheapest of these commodities used in quantity in the pulp and paper mills;

the potential value of this production is $48,000,000. per year.

4. The production units can be constructed in modules, each module producing 10 to 15,000 tonnes/year depending on the commodity being prepared. This minimizes the risks associated with the development of new technology.

5. An opportunity exists for design and construction engineers in New Brunswick to develop unique expertise in the design and construction of these new-technology plants.

RECOMMENDATIONS

We recommend

1. that every effort be made to acquaint decision makers in government and industry with the significance of this promising new technology.

2. that funding be arranged to continue the development of this industrial opportunity, which could have a major impact on the economy of New Brunswick.

   Specifically, that funds be made available for:

   a. preparation of plant cost and cost benefit analyses for the potassium sulphate option and the potassium phosphate option.

      Estimated cost: $30,000. each $ 60,000.

   b. setting up a pilot plant to study plant design, to train operators, and to do further research.

      Estimated cost: $250,000.

c. continuing research in the field at the laboratory level, especially on the sulphite to sulphate transformation, on anion exchange in the phosphate-Pritchard-Fraxon system, and on improvements in calcium rejection in the TVA-type system.

Estimated cost:	$100,000.

3. that a study be done of the opportunities for making sodium chemicals by this technology.

Estimated cost:	$ 15,000.

4. that substantial government assistance be made available to the owners of prototype plant, to support the development of this promising technology and to insure the risks involved in moving into a new area of endeavour.

INTRODUCTION

A. General:

One of the most troublesome problems facing technology today is the collection and disposal of the sulphur dioxide (SO_2) emitted from many industrial sources.

That this problem must be solved is now accepted by almost everyone, as a result of public awareness of the phenomenon called acid rain.

Solution of the problem must be based on one or more of the following premises:

1. cleaning stack gases so that SO_2 is not released into the air. (Without subsequent reuse, this method is costly).

2. collection and reuse. (This method may recover some of the costs).

3. development of technology that will solve the problem by eliminating the production of waste SO_2, in part or altogether.

Methods of scrubbing stack gases that use chemicals, e.g., lime, to absorb SO_2 so that it can be disposed of as landfill are expensive, and plant owners are reluctant to use them. It is not surprising, therefore, that most of the SO_2 recovered from industrial sources is put to use to recover at least part of the cost, smelter gas used to make sulphuric acid (H_2SO_4) for fertilizer production for example.

Many studies of the SO_2 problem have been done on the assumption that, imperfect though it may be, the H_2SO_4 to fertilizer method is the best way to solve the problem. At least this method converts a potential air pollutant to a useful chemical, which can be sold to recover part of the cost. The Kilborn Limited Smelter Sulphuric Acid By-product Feasibility Study was one of these.

This approach concentrates on H_2SO_4, but overlooks an important point: the versatility and potential value of SO_2 itself as a major industrial chemical. It is the thesis of this paper, therefore, that SO_2 is a useful raw material, that can be recovered from stack gases and used directly to make fertilizer and other products.

This paper sets out six ways to use SO_2 directly in fertilizer production. The SO_2 is either bound into the end products or, if left free, is recycled through the plant, eliminating the possibility of air pollution. This paper also shows that these processes are more versatile, may be more effective, and will often produce purer products than processes now in use.

B. Background of This Study:

About twenty-five years ago, at Fraser Cos. Ltd. (now Fraser Inc.) in Atholville, New Brunswick, work began on a method of preparing industrial chemicals using mixtures of a carbonyl compound, sulphur dioxide, and water. In practice, the carbonyl compound was acetone.

This work demonstrated the possibility of making fertilizers and other chemicals without sulphuric acid.

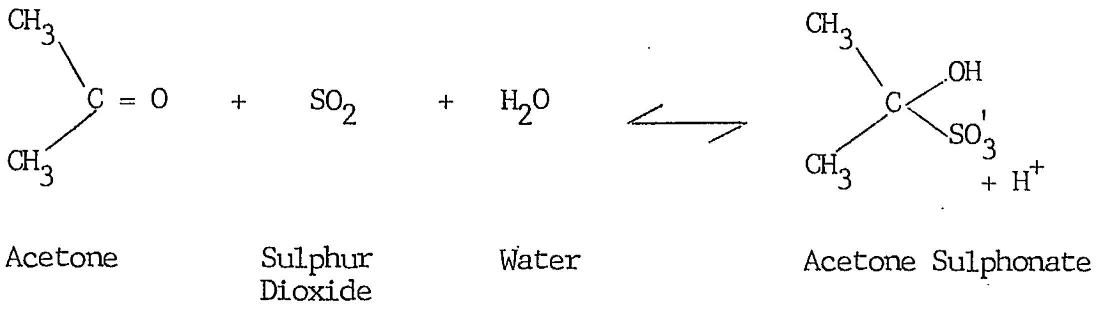
At that time Frasers were looking for a method for recovering base from spent sulphite liquor, and were piloting a base recovery process developed at the Ontario Research Foundation for J. F. Pritchard & Co. of Kansas City, Missouri. This process used 12% SO_2-water solutions to remove ammonium ions from an ion exchanger.

At that same time Abitibi Research was working on a similar process, that used 25% SO_2-water solutions, under pressure.

Neither process was successful, because the volumes of elutant needed to obtain significant levels of recovery were too great to be used in the preparation of cooking acid in some of the conditions existing in sulphite pulping. Also, the economics were doubtful.

When I was assigned to work on the recovery project in 1959, I suggested that the SO_2-water solutions were not generating enough hydrogen ion (H^+) to drive the exchange in favour of regeneration to the H^+ form, and that the addition of acetone or some other carbonyl compound would solve the problem. I reasoned that some of the SO_2 would be converted to an alpha-hydroxysulphonic acid, and that because these are strong acids, we would see an increase in H^+ ion concentration.

Equation:



The success of this concept led to the Pritchard-Fraxon Process for the recovery of sodium and ammonium ions from spent sulphite liquor by ion exchange. Pilot studies demonstrated technical and economic viability.

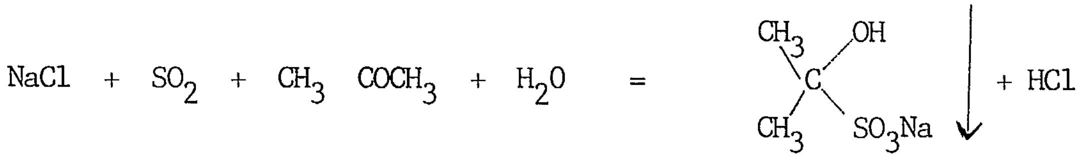
The solvent used in the Pritchard-Fraxon Process was a mixture of 10% acetone, 12% SO_2, 78% water by weight. 99.9% of the acetone was recovered for recycle.

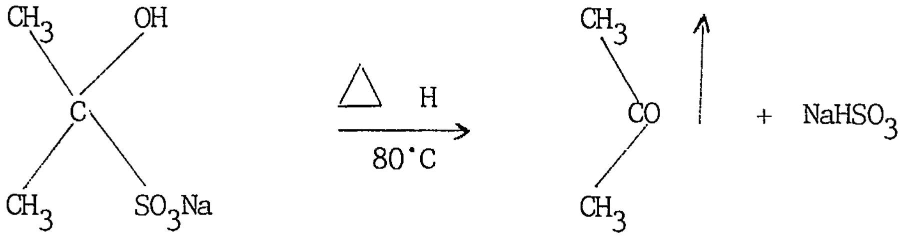
In the course of the development of the Pritchard-Fraxon Process, we tried various combinations of acetone-SO_2-water, and had not worked with these mixtures very long before we realized that they presented several interesting possibilities. For example:

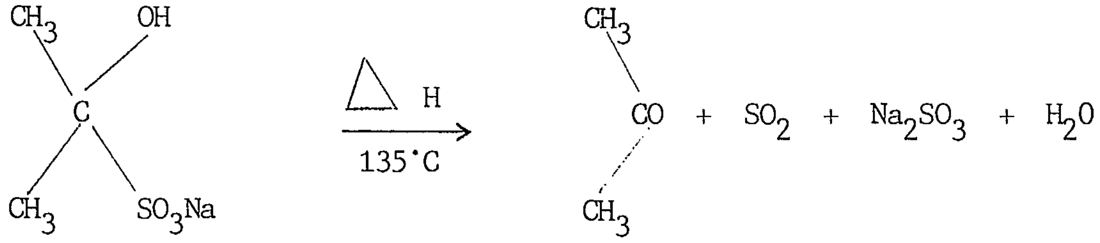
1. the sodium and potassium salts of various acids, <u>including the chlorides</u>, readily converted to the corresponding alpha-hydroxysulphonates, when the powdered salts were shaken with mixtures containing high concentrations of acetone and SO_2.

   Gently heated, these alpha-hydroxysulphonates yielded bisulphites; heated to 135°C they yielded neutral sulphites.

Equations:







Patents: W. J. Wilson U. S. Patent
3,248,278 April 26, 1966
Recovering Monovalent Cations from Spent Sulphite Liquor.

W. J. Wilson, BS Das, Canadian Patent
832,931 January 27, 1970
Production of Alkali Metal Sulphites or Bisulphites

2. certain ore minerals dissolved in these mixtures.

   Generally these were the oxide ores, but there was some indication that zinc sulphide, and possibly some other sulphides, were also attacked.

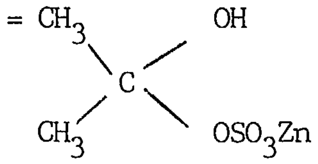
3. some interesting reactions involving multivalent ions were possible.

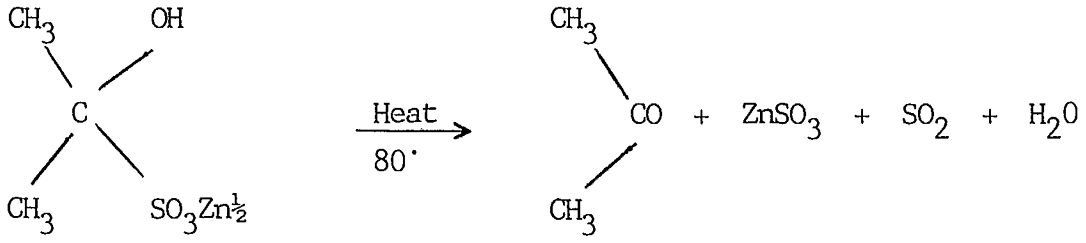
We had noticed, while doing the Pritchard-Fraxon work, that multivalent Metal derivatives precipitated as insoluble sulphites, when free SO_2 was removed from the solutions, and we learned from the literature that the multivalent metal sulphites, except calcium, would readily give up SO_2 and convert to the metal oxide.

This offered a further opportunity to use our discovery: in the processing of multivalent metal ions. For example, zinc recovered from an ion exchanger by the Pritchard-Fraxon method would exist in the form of a precipitate of zinc sulphite, which at about 300°C would convert to zinc oxide.

Equations:

$$ZnO + CH_3\ COCH_3 + SO_2 + H_2O$$



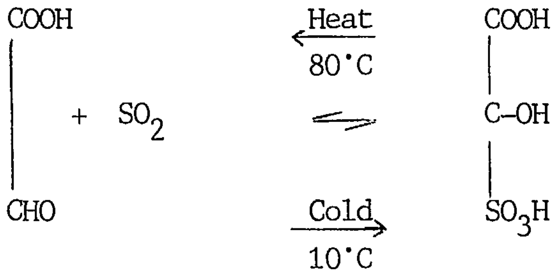


$$ZnSO_3 \xrightarrow[300^\circ]{Heat} ZnO + SO_2$$

4. SO_2-containing gases could be scrubbed using these mixtures.

Independently, some years after our work was done, Spring Chemicals developed a process for recovering SO_2 from gases using glyoxylic acid as the active ingredient. Pure SO_2 could then be recovered by the action of heat.

Equation:



$$\begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{CHO} \end{array} + SO_2 \; \underset{\xrightarrow[10^\circ C]{\text{Cold}}}{\overset{\xleftarrow[80^\circ C]{\text{Heat}}}{\rightleftharpoons}} \; \begin{array}{c} \mathrm{COOH} \\ | \\ \mathrm{C{-}OH} \\ | \\ SO_3H \end{array}$$

5. phosphate rock could be dissolved in these mixtures.

The phosphate rock reaction was studied in some detail, and it was found that calcium could be recovered as calcium acetone-sulphonate while phosphoric acid remained in solution.

This discovery had such obvious application in the fertilizer industry that our work was repeated at the Gulf Research and Development Company laboratories in Merriam, Kansas, where our results were essentially confirmed.

In 1974 I was invited to read a paper on the uses of SO_2 at the Canadian Sulphur Symposium held in Calgary.

Disclosures made at that time led to work by McCullough and Phillips at the National Fertilizer Research Center in Muscle Shoals, Alabama (TVA), where processes were developed for:

1. the manufacture of dicalcium phosphate in good yield with the rejection of surplus lime as calcium acetonesulphonate.

2. the chemical beneficiation of low grade phosphate rock.

Note: Especially important was the substantial reduction of the magnesium content of high dolomitic phosphate rock, which opened the way to more effective use of these deposits; magnesium causes serious problems in the concentration and storage of wet process phosphoric acid.

Patents: McCullough J. F. et al U. S. Patent
4,113,842 September, 1978

Phillips J. F. U. S. Patent
4,238,459 December, 1980

This year Chemical Week February, 1984 has published a release of information showing that something similar to the TVA technique has been used at the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Melbourne, Australia, to manufacture dicalcium phosphate from low grade phosphate rock (17% P_2O_5). This work has shown that crushed phosphate rock can be processed, without pulverizing. There are obvious cost savings to be realized from this possibility; besides, when the rock is highly siliceous, as is the rock the Australians used, there is the added saving of excessive wear of the pulverizers.

A significant amount of technology, therefore, has already resulted from the first work we did at Frasers, but there is no doubt that many possibilities still exist. The Pritchard-Fraxon solvents (P-FS) achieve the effects of strong mineral acids, have a great deal of versatility and wide potential application in chemical manufacturing, and confer special advantages, in that

1. alpha hydroxysulphonates are unstable and easily revert to the bisulphites and the carbonyl compound, which can be volatilized for recovery.

2. bisulphites are soluble in water, but only alkali metal and ammonium sulphites are soluble.

   It happens, therefore, that in a solution that contains calcium bisulphite, heat will drive off SO_2, and the unstable bisulphite will be converted to the sulphite, in a reaction comparable to the bicarbonate to carbonate reaction.

   Alternatively, if a solution contains calcium acetonesulphonate, heat will dissociate the compound, volatilize acetone and SO_2 (including the additional SO_2 needed to convert a sulphite to a bisulphite), and produce calcium sulphite. Calcium sulphite is less soluble than calcium sulphate (gypsum); therefore more complete removal of calcium can be achieved.

3. the normal sulphites (M_xSO_3) have interesting properties. With the exception of the alkali metal sulphites, all of them decompose at fairly low temperatures, the most resistant being magnesium which requires a temperature of 500°C. Dissociation leaves the metal ion oxide and liberates SO_2. In the case of the multivalent ions, therefore, the P-FS system offers a ready route from the dissolved metal ion to the oxide. It is not certain that calcium sulphite can be decomposed completely in this way, but it is known that 90% of the SO_2 can be recovered by calcination in an inert atmosphere at about 1000°C.

4. because H_2SO_3 (sulphurous acid, so-called) is a volatile acid, acidification of sulphites with non-volatile acids makes the recovery of SO_2 fairly easy; and conversions, as, for example, potassium bisulphite to potassium monophosphate by treatment with phosphoric acid, can be achieved.

It would be possible to use a combination of these reactions as the basis of an industrial complex that would manufacture a variety of fertilizer and other chemicals. The processes would use SO_2 and acetone, both of which would be recoverable for recycle, not H_2SO_4, which is not recoverable. In this way the capital cost of an H_2SO_4 plant would be avoided, and because H_2SO_4 is a major raw material in conventional fertilizer manufacture, operating costs would also be lower.

We can show, then, that the Pritchard-Fraxon approach to chemical manufacture offers an important advantage over conventional methods: whereas H_2SO_4 produces sulphates, which are difficult to convert into other chemicals, acetone-SO_2-water mixtures produce sulphites and bisulphites, salts of weak, volatile acids only slightly stronger than carbonic acid, which readily convert to other chemicals when reacted with various acids.

C. Objectives:

Knowing that there were many interesting possibilities inherent in the Pritchard-Fraxon solvents, I approached the Department of Regional Industrial Expansion (DRIE) with the suggestion that a study that would be complementary to the Kilborn Limited Smelter Sulphuric Acid By-Product Feasibility Study should be done, in which it would be demonstrated that the objectives of the Kilborn Study could be achieved without the use of sulphuric acid.

The result of my suggestion was DRIE contract NO. 3124.

The terms of reference were:

APPENDIX A
ATLANTIC ANALYTICAL SERVICES LIMITED
TERMS OF REFERENCE

The consultant will undertake to study the production of fertilizer from SO_2 - acetone - water solutions and investigate expanding this process to a wider range of chemicals. The following items will be addressed:

1. For each of 6 alternative routes to the objectives of this study, produce:

    a) a schematic flow-sheet;
    b) a material balance; and
    c) an energy balance

2. The 6 alternatives are: potassium chloride to potassium bisulphite, by ion exchange and by double decomposition; phosphate rock to phosphoric acid by the same approaches; and the TVA calcium monophosphate process; and acidulation of phosphate rock using by-product hydrogen chloride.

3. References will be made to appropriate sources; particularly the Tennessee Valley Authority (TVA), Muscle Shoals, Alabama and C/S Assoc., Oak Ridge, Tennessee.

4. Conduct limited experimental work on the solubility of calcium and potassium bisulphite, and phosphate rock in acetone - SO_2 - water mixture of approximately 25% acetone, 25% SO_2 and 50% water by weight.

5. Identify any economically viable market possibilities for any of the alternative processes.

6. Produce 10 copies of a final report summarizing the work, conclusions reached, recommendations and identify further areas for follow up.

Two changes were agreed upon after the work had begun:

1. a visit to the TVA Research Center in Alabama revealed that the TVA process produced dicalcium phosphate, not monocalcium phosphate, and it was agreed that the actual TVA process should be discussed in this paper.

2. it became clear that the hydrochloric acid formed during the preparation of potassium bisulphite from potassium chloride should be the starting point for the HCl process, not some other source of acid, and it was agreed that this fact should be considered in this paper.

THE PROCESSES

A. General:

Six possible processes for meeting the objectives of this study are presented. The unique advantages and the potential products of each process are considered.

A number of matters common to two or more of the processes are discussed first, to avoid repetition:

1. Raw Materials

    a. Potassium chloride (KCl), known in the industry as muriate of potash

    Approximate analysis:

K_2O	60.5%
KCl	96.0%
NaCl	3.0%
Insolubles	0.75%
Ca	Trace
Mg	Trace
Bromine	100 ppm

Note: KCl would be procured from the New Brunswick potash mines.

The KCl would have to be dissolved and filtered before use to remove insoluble impurities. There would be a soluble impurity as well, about 1% of sodium chloride, which would carry through the whole process, and the sodium salt would be a co-product with the potassium salt.

b. Phosphate Rock

Analysis.	BL-26
P_2O_5	33.3%
CaO	49.0%
MgO	0.27%
Al_2O_3	1.10%
Fe_2O_3	1.20%
CaF_2	3.90%
SiO_2	4.30%

Note: Phosphate rock comes in many grades and purities, and it would be the task of the plant managers to evaluate possible sources of rock for use in particular operations.

For purposes of this paper, we have chosen the rock described in TVA publications as BL-26. This is a rock from central Florida that has the above analysis. Rocks that could be used in our processes, however, could be dolomitic or low grade rocks not suitable for the manufacture of phosphoric acid by the wet process. These might offer economic advantages.

It is assumed here, also, that the rock used would be ground to - 100 mesh, but a recent trial in our laboratory suggests that it would be possible to use coarse rock, such as that received by Belledune Fertilizer, if a counter-current process were used.

More experimental work would be needed to confirm this possibility but work done in Australia demonstrated that the P-FS system could handle coarse material and thus save the very considerable costs of pulverizing the rock.

c. Sulphur Dioxide (SO_2)

Note: The SO_2 solutions used in our studies of the Pritchard-Fraxon solvents have always been derived from the burning of elemental sulphur to produce burner gas of approximately 18% SO_2.

Absorption was 2-stage: the gas first contacted the acetone still overheads, at least 95% acetone, which is an excellent absorbent for SO_2; makeup water was then added to knock down any acetone carried into the gas stream.

This process was remarkably effective, and losses of SO_2 and acetone were negligible.

Other sources of sulphur are also available in New Brunswick and might be used, depending on plant location. A similar burning operation using pyrite to give 12% SO_2, or 6-7% smelter gas, would be equally acceptable for SO_2 recovery; but when we drew up our energy balances for this paper we assumed that elemental sulphur would be used, because we also assumed that a plant would be located near the potash and lime deposits in the south of the province.

Noranda's decision not to proceed with the zinc smelter that was planned for northern New Brunswick makes the use of elemental sulphur even more likely, because this means there will be no uncommitted smelter gas in the province. Elemental sulphur is produced at the Irving refinery.

d. Acetone

Note: The acetone used is the commercial grade product. It is made in Montreal.

e. Lime

Note: The lime used is run-of-the-kiln quick lime.

Depending on the quantity needed, Havelock might be able to meet the requirement; or it might be necessary to set up an additional kiln, most likely to burn lime from the Nauwigewauk deposits.

2. Ion Exchange

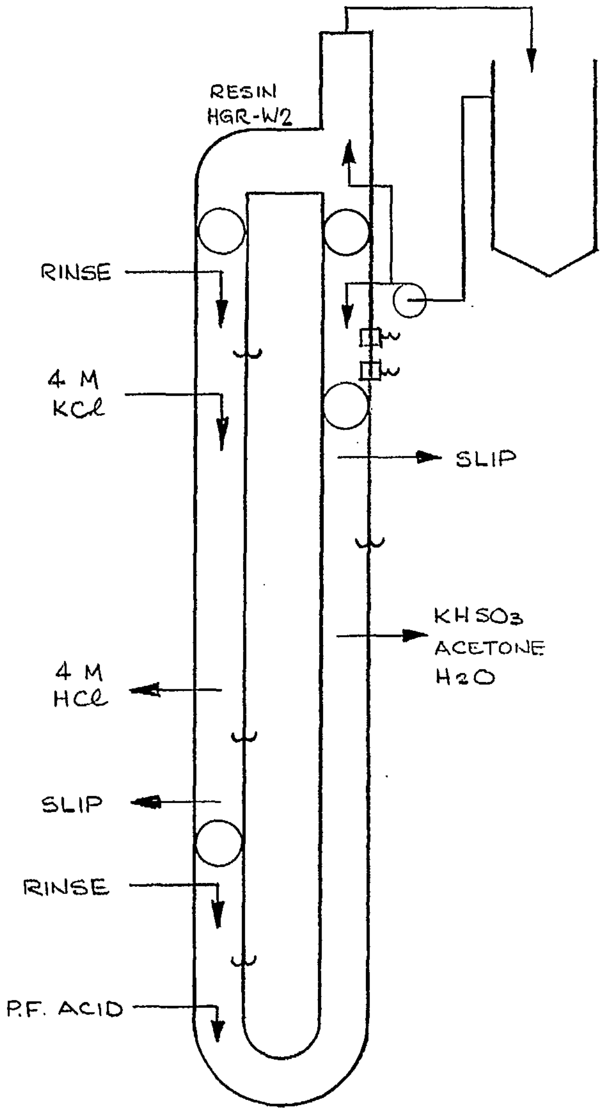
The ion exchange system suggested for use in the process discussed in this paper is the Higgins Contactor, made by C/S Associates Inc. of Oak Ridge, Tennessee.

The Higgins Contactor is a continuous ion exchange system in which the resin is pulsed around a loop countercurrently to in-coming solutions. From time to time valves open and a slug of resin changes its position in the loop. The loop is specifically redesigned for each new use to make sure that denser solutions are at low points, to avoid having dense solutions falling through the column into less dense solutions, washwaters, etc. As the resin moves around the loop, it periodically reaches a point where it is removed and reclassified, then returned to the system.

A schematic diagram of the sequence for the potassium chloride-potassium bisulphite system is shown in Figure I.

FIGURE I

CCIX - CONVERSION OF KCl TO KHSO$_3$



The Higgins Contactor has been used extensively for many years in demineralizing, in water treatment, and in chemical recovery. Especially significant for the processes under discussion here is the fact that these units have operated effectively at nitrate plants, some for over ten years, recovering ammonia from waste waters by the regeneration of cations with 4M nitric acid, giving a product solution containing 25-35% ammonium nitrate.

At Atlantic Analytical, in the late 70's, we built one of these units (manually operated) and used it to study chemical recovery from concentrated spent sulphite liquor. This work was very successful. As well, I have discussed the processes proposed here with Dr. Higgins and others at C/S Assoc. and obtained data from them on the productivity and maximum size of the units.

Because the ion exchanging processes proposed in this paper are simple ones and well understood; and because of all the experience in the field, that has been gained over many years, and all the data already available, a New Brunswick project could go to the design stage with a minimum of pilot plant expenditure.

Note: Another continuous ion exchange system exists. It is produced by Himsley Engineering of Toronto and has been used in resin-in-pulp systems in the uranium industry. Our work on spent sulphite liquor, however, seemed to show that the Higgins Contactor achieved our objectives more effectively. At some time, no doubt, Himsley Engineering should be approached to see if they can meet our requirements, but for the moment we are considering only the proven process.

3. Material Balances

Material Balances presented here are based on 1000 units of the commodity being processed; that is, the potassium bisulphite balances start with an input of 1000 units of KCl, and the phosphate processes start with an input of 1000 units of P_2O_5. This is to simplify later correlations when we have to consolidate the different processes into a consistent production plan.

All values are based on weight.

B. The Potassium Processes:

1. Potassium Bisulphite by Ion Exchange

The steps of the process are:

1. potassium chloride (KCl) is dissolved in water to give a 4M solution, and after being filtered is passed to the loading side of the ion exchanger. Potassium ions (K^+) replace hydrogen ions (H^+) on the resin, and the effluent is hydrochloric acid (HCl) approximately 4M.

Note: Possibly about 1% of the potassium will appear as leakage in the effluent, but this will be recovered and recycled later if the HCl is concentrated for sale; otherwise it will appear in the KCl by-product.

2. the K^+ loaded resin is then passed to the stripping side of the ion exchanger, where it is contacted with an eluent containing 18% acetone, 20% SO_2, and the rest water. The amount of the eluent is 1.25 times the stoichimetric amount required for the K^+ in the circuit.

3. the eluent from the stripping side of the exchanger contains the recovered K^+ and the acetone, SO_2, and water.

   This stream is passed to an SO_2 stripper, entering at about 20°C, and is stripped of its free SO_2 content.

   The stripper overheads are the SO_2 not combined with the K^+ to give potassium bisulphite ($KHSO_3$). In fact, slightly more SO_2 is stripped than meets the strict $KHSO_3$ formula, the mixture having a small amount of the sulphite present, as K_2SO_3. Also, a small amount of acetone in water accompanies the overheads.

4. the stripper bottoms, coming from the stripper reboiler at about 86°C, are passed to an acetone still, where the acetone is recovered, giving an overhead that contains 99.9% of the acetone that was in the feed, plus minor amounts of water and SO_2.

5. the acetone still bottoms are approximately 29% by weight of $KHSO_3$, which can then be passed for further processing to make the desired end-products.

   The solubility of $KHSO_3$ is 31% by weight at 15°C.

Note: The acetone still overheads are 65-85°C, and the acetone still reboiler temperature is 100°C. These temperatures are about the same in all stripper and acetone still operations.

Depending on what the end-product is to be, it may be possible to recover the product without totally distilling all the acetone, which would result in energy savings, but until the product mix is finalized, this aspect cannot be considered.

The largest countercurrent ion exchanging (CCIX) unit that C/S Assoc. has built so far is 4 feet in diameter. Assuming that resin moves through the column at 6 inches per minute, and that the resin utilization capacity is 1.8 equivalents per minute, production would be 38.6 kilograms per minute of $KHSO_3$, or 19,400 tonne per year assuming a 350 day operating year. This would mean production per unit of approximately 14,000 tonne per year, if the product were all converted to potassium sulphate (K_2SO_4).

Following are:

1. Schematic Flowsheet: Figure II
2. Material Balance: Table 1
3. Energy Balance: Table 2

FIGURE II

POTASSIUM BISULPHITE ION EXCHANGE SYSTEM

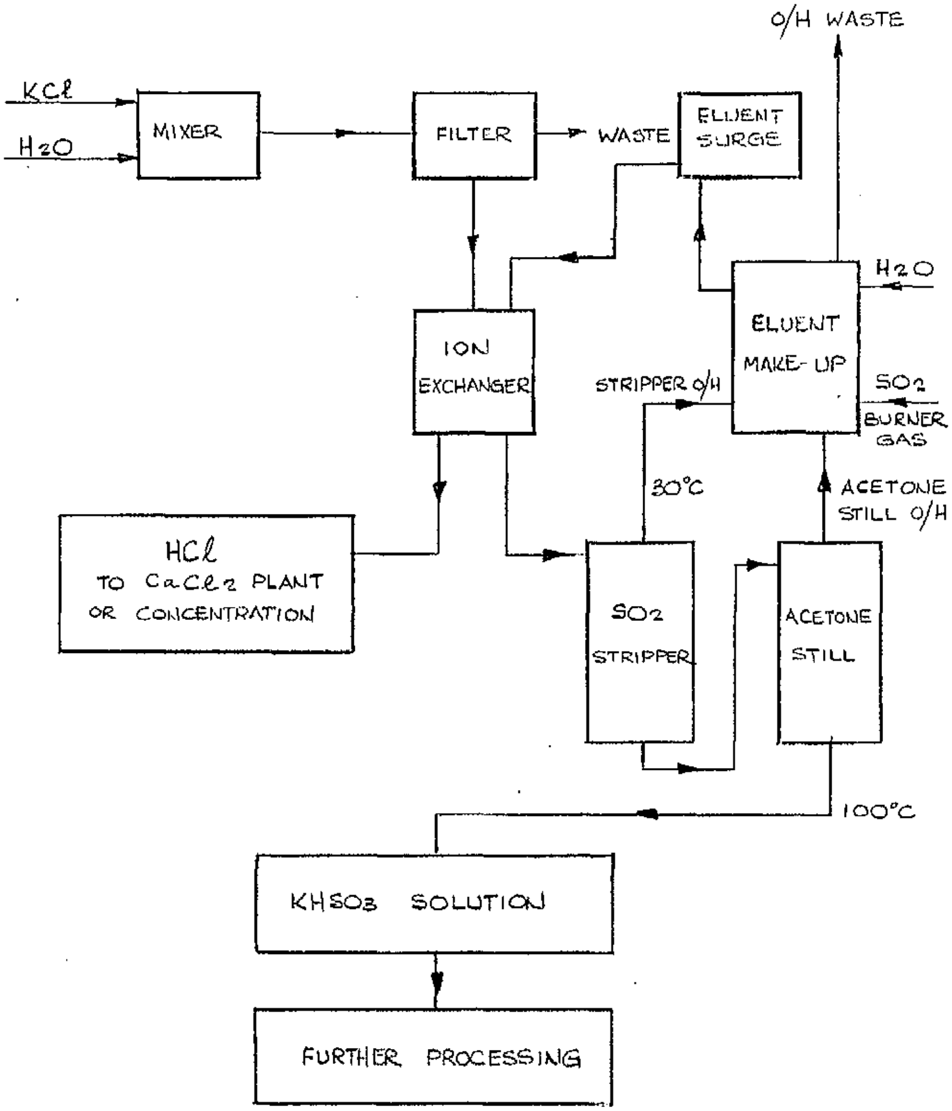


TABLE 1

Potassium Bisulphite by Ion Exchange

Material Balance

Units Kg/hr

	K^+	Na^+	KCl	NaCl	H_2O	HCl	SO_2	Acetone
Loading								
Potassium Chloride	—	—	1000	20	3363	—	—	—
Eluent	—	—	—	—	3353	—	1072	972
Elution (1)	—	—	10	—	3363	496	—	—
(2)	514	8	—	—	3353	—	1072	972
SO_2 Stripper								
Feed	514	8	—	—	3353	—	841 Combined 231 Free	972
O/H	—	—	—	—	2	—	252	19
Bottoms	514	8	—	—	3351	—	820	953
Acetone Still								
Feed	514	8	—	—	3351	—	820	953
O/H	—	—	—	—	74	—	4	952
Product Bottoms	514	8	—	—	3277	—	816	1

TABLE 1 Continued

Eluent Makeup	SO_2	Acetone	H_2O
Recycle SO_2 Stripper O/H	252	19	2
Recycle Acetone Still O/H	4	952	74
Recycle SO_2 ($CaCl_2$ unit)	384	—	—
Total Recycle	640	971	76
Makeup	432 (S = 216)	1	3277

Note

Water and Acetone Still O/H recycles are used to scrub SO_2 in the SO_2 tower.

Product	1580 Kg/hr $KHSO_3$ as a 32.1 Wt% solution

TABLE 2

Potassium Bisulphite by Ion Exchange
Energy Balance

Production	1580 Kg/hr	$KHSO_3$ as a 32 Wt% solution

Process Requirements		K cal/hr
SO_2 Stripper	+	267,885
Acetone Still	+	244,748
Recovery		
75% Heat of Vaporization	–	144,351
Sulphur Burning	–	921,264
Nett Input	–	552,982

2. Potassium Bisulphite by Heterogeneous Reaction

When mixtures of acetone, SO_2, and water containing high levels of acetone (about 60% by weight) are shaken with sodium chloride, a heterogeneous reaction ensues, which gives insoluble sodium acetonesulphonate as the only solid phase.

Equation:

$$\text{NaCl} + SO_2 + \text{Acetone} + H_2O = \text{Na acetone sulphonate} + \text{HCl}$$

The discovery of this reaction at Frasers in the early 60's led us to experiment with alkali metal and ammonium salts, and our work proved that this was a general reaction.

We then discovered that on mild heating (60-80°C), the acetonesulphonates converted to the bisulphites, and that on more vigorous heating (135°C), they formed neutral sulphites (M_2SO_3).

This process for manufacturing alpha-hydroxysulphonates was patented. Most of the work described in the patent was done on sodium chemistry, but enough was done to show that potassium compounds could be prepared with equal facility.

The Heterogeneous Reaction offers very interesting possibilities, but it has been demonstrated only on the bench top. Refining of the techniques and pilot plant development would be necessary before a plant based on this concept could be built.

The steps of the process are:

1. KCl is purified to remove insolubles by saturating the makeup water with KCl.

2. the solvent (approximately 65% acetone, 15% SO_2, and 20% water) is brought into intimate contact with the purified KCl, and the heterogeneous reaction is allowed to proceed.

   In industrial practice, a countercurrent system would be used.

3. the resulting alpha-hydroxysulphonate slurry is filtered.

4. the filter bottoms are directed to an SO_2 stripper; the cake goes to a decomposer.

5. in the decomposer, the alpha-hydroxysulphonate is converted to bisulphite or sulphite (depending on temperature), or it is reacted with acids to produce other potassium salts.

6. the acetone and SO_2 in the overheads from the decomposer are returned to the system.

NOTE: Because a countercurrent system is used, the feed to the decomposer contains very little HCl; the filter bottoms contain the HCl generated by the reaction, as well as any unreacted KCl and the excess acetone-SO_2-water solvent.

7. the filter bottoms are fed to an SO_2 stripper and stripped of SO_2 and minor amounts of acetone and water.

8. the stripper bottoms are fed to an acetone still, where the acetone and the remaining SO_2 are recovered, leaving an aqueous solution of HCl and KCl.

   Under these conditions the KCl precipitates and can be removed for recycle. The acid, which is about 18% by weight, can be removed at this point.

NOTE: If we were to produce calcium chloride ($CaCl_2$), there is a possibility that the reaction would have taken place and the product could have been removed before the stripper bottoms were fed to the acetone still.

The HCl product can be used in one or more of three ways:

1. the solution can be concentrated to a saleable level and the result sold as the acid.

2. the HCl in the acetone still or stripper bottoms can be reacted with lime in slight excess, then evaporated to recover $CaCl_2$.

NOTE: It would be necessary to ensure that the reaction went to completion to avoid losing KCl.

3. any or all filter, acetone still, and stripper bottoms can be reacted with phosphate rock to produce phosphoric acid.

NOTE: The acetone-SO_2-water mixture, as it would exist in the filter bottoms, has not been tested for reactivity with phosphate rock, or to determine what the insoluble stage might be in consequence of the reaction, but it seems logical to suggest using the effluent at this stage rather than waiting till after heat has been expended to recover SO_2 and acetone. Energy savings seem possible, although SO_2 and acetone would have to be recovered at some stage, and energy savings might not be significant.

Following are:

1. Schematic Flowsheet: Figure III.
2. Material Balance: Table 3
3. Energy Balance: Table 4

FIGURE III

POTASSIUM SULPHITE / BISULPHITE HETEROGENOUS SYSTEM

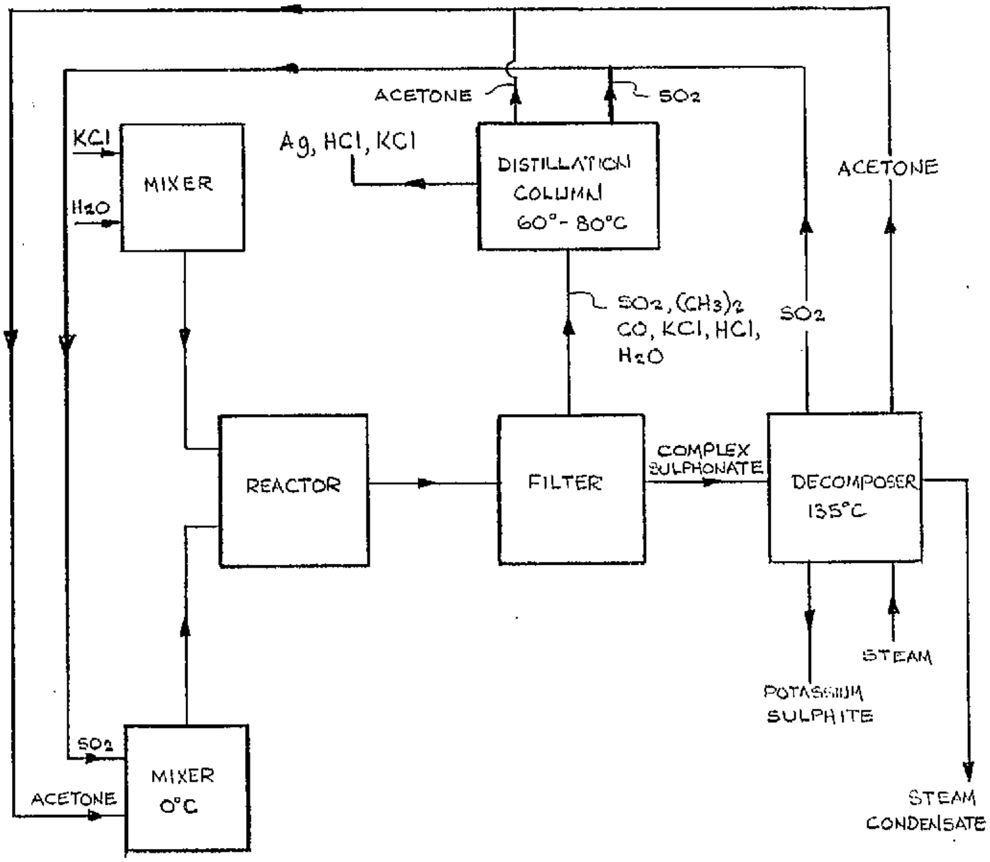


TABLE 3

Potassium Bisulphite - Heterogeneous System

Material Balance

Units Kg/hr

Reactor

Feed		KCl	SO_2	Acetone	H_2O	
Recycles						
Acetone Still Bottoms Filtrate		100	---	---	---	
Acetone Still O/H		---	22	10733	870	
SO_2 Stripper O/H		---	2042	160	16	
Decomposer O/H		---	82	1095	345	
Total Recycle		100	2146	11988	1231	
Makeup						
KCl		1000	---	---	2169	
Solvent		---	854	12	---	
Total Reactor Feed		1100	3000	12000	4000	
No 1 Filter						HCl
Feed		1100	3000	12000	4000	
Bottoms		100	2062	10903	3653	490
	K^+					
Cake	524	---	938	1097	347	

TABLE 3 Continued

		KCl	SO_2	Acetone	H_2O	HCl
SO_2 Stripper						
Feed		100	2062	10903	3653	490
O/H		---	2042	160	16	---
Bottoms		100	20	10743	3637	490
Acetone Still						
Feed		100	20	10743	3637	490
O/H		---	20	10733	870	---
Bottoms		100	--	10	2767	490
Decomposer						
	K^+					
Feed	524	---	938	1097	347	---
O/H	---	---	82	1095	345	---
Product Cake	524	---	856	2	2	---

Product 1609 Kg/hr $KHSO_3$ solids

or 1060 Kg/hr K_2SO_3 solids

TABLE 4

Potassium Bisulphite - Heterogeneous System

Energy Balance

1060 Kg/hr K_2SO_3 Solids

		K cal/hr
Process Requirements		
SO_2 Stripper	+	797,255
Acetone Still	+	2,070,094
Decomposer	+	420,120
Heat Recovery		
75% Heat of Vaporization	-	1,472,765
Sulphur Burning	-	921,224
Nett Input	+	894,080

Note Process requirements for 32% $KHSO_3$ solution are + 789,050

C. The Phosphate Processes:

1. The TVA Dicalcium Phosphate Process

The main thrust of the Pritchard-Fraxon research, and also of the studies done at the Gulf Research Center, was to prepare phosphoric acid by the precipitation of all the lime in the phosphate rock as calcium acetonesulphonate.

At TVA, McCullough and Phillips took a different approach. After we had made public the potential of the acetone-SO_2-water solvents at the Calgary Sulphur Symposium, they worked on the production of dicalcium phosphate. Their work was most comprehensive and provides a solid base of data, which greatly extends our knowledge of the field.

NOTE: Dicalcium phosphate is an excellent fertilizer, popular in many countries, e.g., Brazil, and although not much used in North America, is a marketable commodity.

The process proceeds as follows:

1. -100 mesh phosphate rock is fed countercurrently to the solvent with most of the SO_2 entering independently of the liquid phases.

   The solvent is 35% acetone, 20% SO_2 and 45% water by weight.

   A small amount of calcium is present in the recycle streams as calcium bisulphite or calcium acetonesulphonate. This remains in solution during the precipitation of the dicalcium phosphate.

2. the solid-phase calcium acetonesulphonate emerges from the reactor along with the insoluble gangue minerals, and contains about 30% of the lime, 90% of the aluminum, 80% of the fluoride, 70% of the iron, and 40% of the magnesium.

3. this solid-phase material is filtered and washed and approximately 97% of the P_2O_5 is recovered in the filtrate.

4. the solid is fed to a decomposer, where it is heated to a temperature of 135°C to recover sulphur and acetone for recycle. About half of the combined sulphur is recovered, and all of the acetone.

   An impure residue, consisting largely of calcium sulphite, remains.

5. the filter and washer bottoms are combined and fed to an SO_2 stripper, where free SO_2 is removed.

   Removal of the SO_2 leads to the precipitation of fairly pure dicalcium phosphate.

   The overheads contain small amounts of acetone and water and all of the free SO_2.

   The stripper bottoms are a slurry of dicalcium phosphate.

6. the stripper bottoms slurry is then fed to another filtering and washing system and emerges as wet dicalcium phosphate cake.

7. the filter and washer bottoms from this operation, which are largely acetone and water with some lime and a little SO_2, are sent to the acid makeup system, thence to recycle.

8. the dicalcium phosphate is then ready to be dried and sold as a fertilizer, or, by acidulation, it can be used as a source of phosphoric acid (H_3PO_4).

This appears to be a straightforward process. The reactions take three or four hours to occur in the countercurrent reactor and should not present any serious difficulties.

Following are:

1. Schematic Flowsheet: Figure IV
2. Material Balance: Table 5
3. Energy Balance: Table 6

FIGURE IV

DICALCIUM PHOSPHATE
T.V.A. SYSTEM

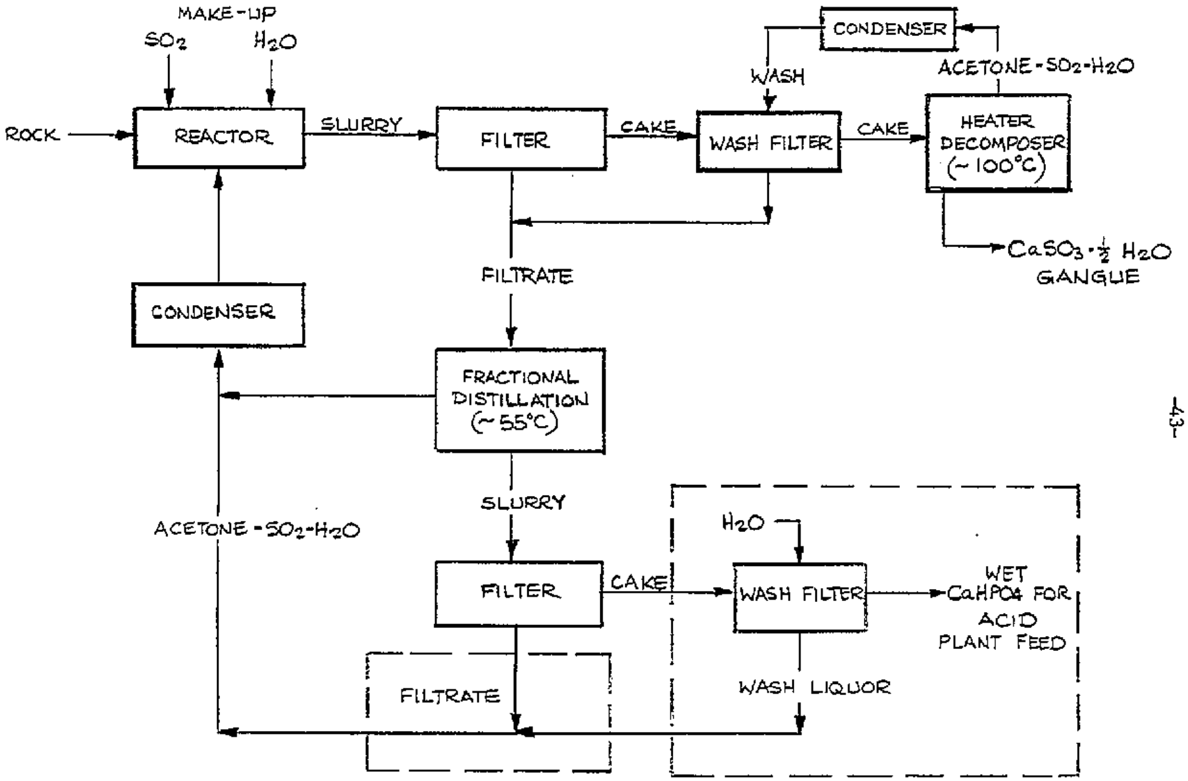


TABLE 5

TVA $CaHPO_4$ Process

Material Balance
Units Kg/hr

	P_2O_5	CaO	SO_2	Acetone	H_2O
Reactor					
Rock	1000	1470	----	----	----
No 2 Filter Bottoms	----	100	228	6508	8510
No 2 Washer Bottoms	----	47	110	128	370
Stripper O/H	----	----	2857	360	7
Makeup	----	----	805	4	113
Total Input	1000	1617	4000	7000	9000
No. 1 Filter					
Feed	1000	1617	4000	7000	9000
Bottoms	840	763	1538	4191	6761
Cake	160	854	2462	2809	2239
No. 1 Washer					
Feed	160	854	2462	2809	2239
Wash	----	----	805	1458	284
Bottoms	130	150	1657	2807	2126
Cake	30	704	1610	1460	397
Decomposer					
Feed	30	704	1610	1460	397
O/H	----	----	805	1458	284
Cake	30	704	805	2	113

TABLE 5 Continued

	P_2O_5	CaO	SO_2	Acetone	H_2O
Stripper					
No 1 Filter Bottoms	840	763	1538	4191	6761
No 1 Washer Bottoms	130	150	1657	2807	2126
Total Feed	970	913	3195	6998	8887
O/H	----	----	2857	360	7
Bottoms	970	913	338	6638	8880
No 2 Filter					
Feed	970	913	338	6638	8880
Bottoms	----	100	228	6508	8510
Cake	970	813	110	130	370
No 2 Washer					
Feed	970	813	110	130	370
Wash	----	----	----	----	370
Bottoms	----	47	110	128	370
Product Cake	970	766	----	2	370

Product 1736 Kg/hr $CaHPO_4$ at 17.5% H_2O content.

TABLE 6

TVA Dicalcium Phosphate Process
Energy Balance

Production 1736 Kg/hr $CaHPO_4$ at 17.5 H_20 Content

Process Requirements		K cal/hr
Decomposer	+	580,534
SO_2 Stripper	+	1,096,745
Recovery		
75% Heat of Vaporization	-	553,304
Sulphur Burning	-	909,974
Nett Input	+	214,000

2. Phosphoric Acid by Ion Exchange

In anion exchange, phosphoric acid can be used as a monobasic acid. It appears, therefore, that it might be better to use anion exchange than the cation exchange that we suggest. The ion exchanger, however, would have to be regenerated with about 1.25 M of regenerant per M of phosphoric acid (H_3PO_4), which would severely limit the process, because it would produce H_3PO_4 contaminated with non-volatile acids, such as H_2SO_4 or HCl. The use of hydroxyl ion would not be practical either, because of the cost of hydroxide.

The only practical anions to use would be the bisulphite or alpha-hydroxysulphonate ions. We have no experience, however, of the performance of these in H_3PO_4. Accordingly, although anion exchange is a possibility and might be worth studying sometime, in this paper we will discuss only the production of H_3PO_4 by cation exchange.

The TVA analysis of phosphate rock that we are using for discussion purposes, shows that calcium oxide is present in excess of the amount required to form tricalcium phosphate. The efficiency of the exchanger being directly dependent on the amount of calcium ion (Ca^{++}) to be exchanged, any step that reduces the amount of Ca^{++} ion to be exchanged will lead to greater efficiency in the use of the exchanger. In the TVA dicalcium phosphate process, approximately one third of the calcium does not go into solution, but is removed as a cake by filtration and washing. In this way, a third more rock can be processed in any given exchanger. This approach is incorporated into our flowsheet.

Higgins indicates that C/S Assoc. has successfully purified H_3PO_4 by the cation exchange of 30% P_2O_5 acid. Given the dissociation constant of H_3PO_4, we thought that such mixtures would be very poor generators of H^+ ion, which in the presence of a strong acid, would be essentially unionized. Accordingly, we measured the effect of adding H_3PO_4 to a simulated ion exchanger effluent and obtained the following results, which indicate that the extra H_3PO_4 did not lead to much change in pH.

Results of our experiments:

Wt % H_3PO_4	pH
0	0.35
5	0.23
10	0.15
15	0.10
20	0.05

We therefore propose in the flowsheet that the decationized filtrate from the rock dissolution stage be recycled after fortification with SO_2 and acetone to attack another batch of rock. After appropriate ion exchange this will leave a concentration of P_2O_5 in the decationized product double that found in a system in which no recycle has been incorporated. By this step the cost of acetone distillation can be halved.

The process proceeds as follows:

1. the solvent (35% acetone, 20% SO_2, and 45% water) and the recycled H_3PO_4 are allowed to react with phosphate rock.

2. the resulting slurry is filtered and washed.

3. filtrate and washings are passed through an ion exchanger in the H^+ form.

4. the effluent from the exchanger contains the H_3PO_4, which can be recycled or sent for H_3PO_4 recovery.

5. the stream sent to recovery is passed first to an SO_2 stripper, where most of the SO_2 is recovered, and then to an acetone still, where 99.9% of the acetone is recovered.

6. the product then contains approximately 19% P_2O_5 by weight, which can be further concentrated, or reacted to form other products.

7. the cake from the filters and washers is heated to 135°C at which time any free acetone and SO_2 are recovered for recycle.

8. the ion exchanger, now in the Ca^{++} form, is eluted with acetone-SO_2-water solvent. This converts the exchanger to the H^+ form, and produces an effluent of acetone-SO_2-water, which contains the calcium.

9. this effluent is passed to another SO_2 stripper, where most of the SO_2 is removed and calcium sulphite precipitates.

10. the precipitate is filtered and washed.

11. the filtrate is sent to the SO_2 makeup system.

    It is not necessary to distill the acetone, because the calcium sulphite is insoluble, once excess SO_2 has been stripped from the solution.

Because the H_3PO_4 is prepared by ion exchange , it should be exceptionally pure and should be suitable for use in making food grade acid and liquid fertilizer. There would be none of the problems associated with the precipitation of inorganic phosphates in the concentrated acid, which is a major difficulty in the production of superphosphoric acid (70%) from wet process acid.

Following are:

1. Schematic Flowsheet: Figure V
2. Material Balance: Table 7
3. Energy Balance: Table 8

FIGURE V

PHOSPHORIC ACID
ION EXCHANGE SYSTEM

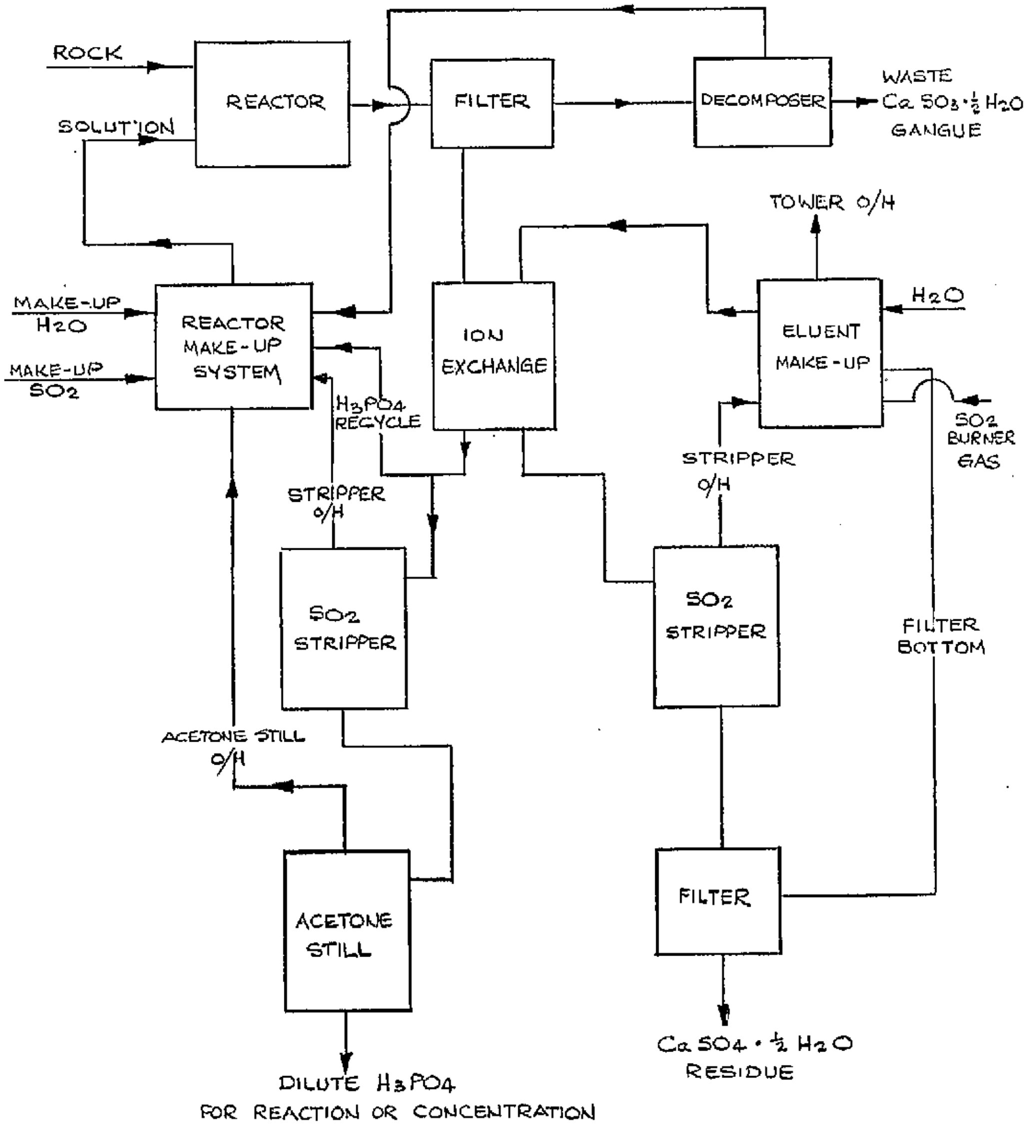


TABLE 7

Phosphoric Acid by Ion Exchange

Material Balance

Units Kg/hr

	P_2O_5	CaO	SO_2	Acetone	H_2O
Reactor					
Rock	1000	1470	----	----	----
P_2O_5 Stripper O/H	----	----	1314	90	20
P_2O_5 Acetone Still O/H	----	----	50	2822	160
Cake Recovery O/H	----	----	636	1283	448
P_2O_5 Recycle	970	----	1363	2923	4231
Makeup	----	----	717	21	8552
Input					
Reactor	1970	1470	4000	7000	9000
No 1 Washer	----	----	80	140	180
Total	1970	1470	4080	7140	9180
No 1 Filter					
Feed	1970	1470	4000	7000	9000
Bottoms	1655	763	2344	5466	7456
Cake	315	707	1656	1534	1544
No 1 Washer					
Feed	315	707	1656	1534	1544
Wash	----	----	80	140	180
Bottoms	285	150	383	381	1006
Discard Cake	30	557	273	1293	538

TABLE 7 Continued

	P_2O_5	CaO	SO_2	Acetone	H_2O
Ion Exchange P_2O_5 System					
IXR Feed					
No 1 Filter Bottoms	1655	763	2344	5466	7456
No 1 Washer Bottoms	285	150	383	381	1006
Total	1940	913	2727	5847	8462
IXR Effluent	1940	----	2727	5847	8462
P_2O_5 Recycle	970	----	1363	2923	4231
Cake Recovery					
Feed	30	557	1273	1293	538
O/H	----	----	636	1283	448
Sulphite Cake	30	557	637	10	90
P_2O_5 Recovery System					
SO_2 Stripper					
Feed	970	----	1364	2924	4231
O/H	----	----	1314	90	20
Bottoms	970	----	50	2834	4211
Acetone Still					
O/H	----	----	50	2822	160
Bottoms 970	970	----	----	12	4151

Product 5133 Kg/hr at 19 Wt% P_2O_5 solution

TABLE 8

Phosphoric Acid by Ion Exchange
Energy Balance

Production 5133 Kg/hr 19 Wt% P_2O_5 Solution

Process Requirements		K cal/hr
Decomposer	+	462,088
SO_2 Stripper	+	502,035
Acetone Still	+	576,767
Heat Recovery		
75% Heat of Vaporization	–	682,092
Sulphur Burning	–	720,302
Nett Input	+	138,496

3. Phosphoric Acid by Heterogeneous Reaction

My early work showed that we could produce H_3PO_4 by direct heterogeneous reaction, with the advantage over conventional methods that most of the lime could be recovered as insoluble alpha-hydroxysulphonate. The solvent used contained about 65% acetone, 25% SO_2, and 10% water by weight; the product was a dilute solution of H_3PO_4 (about 5% P_2O_5 by weight). The acetone-SO_2-water system has been studied in three laboratories: Frasers Gulf, and TVA, and a 3-component diagram has been prepared in each, but the diagram prepared at the TVA is the most complete of the three and is included here. X indicates a composition of the filtered stream without regard to the lime and P_2O_5 content and shows it to be rich in acetone and located in the acetone-rich, single phase region. Not much work has been done in this area, however, and considerable refining of the technique would be needed to optimize results.

My early work having shown that further addition of SO_2 would bring a solution such as the reactor effluent into the 2-phase region, comprised of a water-rich phase and an acetone-SO_2-rich phase (70% by weight of the P_2O_5 being in the water-rich phase, it follows that the water-rich phase would be the only one that would have to be processed to recover H_3PO_4. Early work also having shown that only 10% of total acetone was present in the water-rich phase, considerable heat savings would be realized, and these would be a high concentration of H_3PO_4 in the still bottoms.

Both of these approaches are presented here:

a. Direct Stripping

The process proceeds as follows:

i. the rock is reacted with the solvent, and a solution phase and a solid phase result.

ii. after filtration the cake is passed to a decomposer, where acetone and SO_2 are recovered by heating to 135°C. The residue is calcium sulphite $\cdot 5\ H_2O$ and gangue.

Note: The cake need not be washed, because the exchange system used would be countercurrent, in which the cake would be contacted only by in-coming solvent.

iii. the filtrate is passed first to an SO_2 stripper and then to an acetone still for recovery of SO_2 and acetone.

iv. the still bottoms are an aqueous solution of H_3PO_4.

Note: 1. In the example cited, the concentration of H_3PO_4 is 41% P_2O_5 by weight. If a higher rate of reaction were required, however, more water would be needed and the concentration would be lower.

Note: 2. The acid will contain some calcium, because complete precipitation is not achieved.

v. all other streams return to the solvent makeup system.

vi. the H_3PO_4 can be concentrated and recovered, or used in further reactions.

Following are:

1. Schematic Flowsheet: Figure VI
2. Material Balance: Table 9
3. Energy Balance: Table 10

FIGURE VI

PHOSPHORIC ACID HETEROGENOUS REACTION
DIRECT STRIPPING

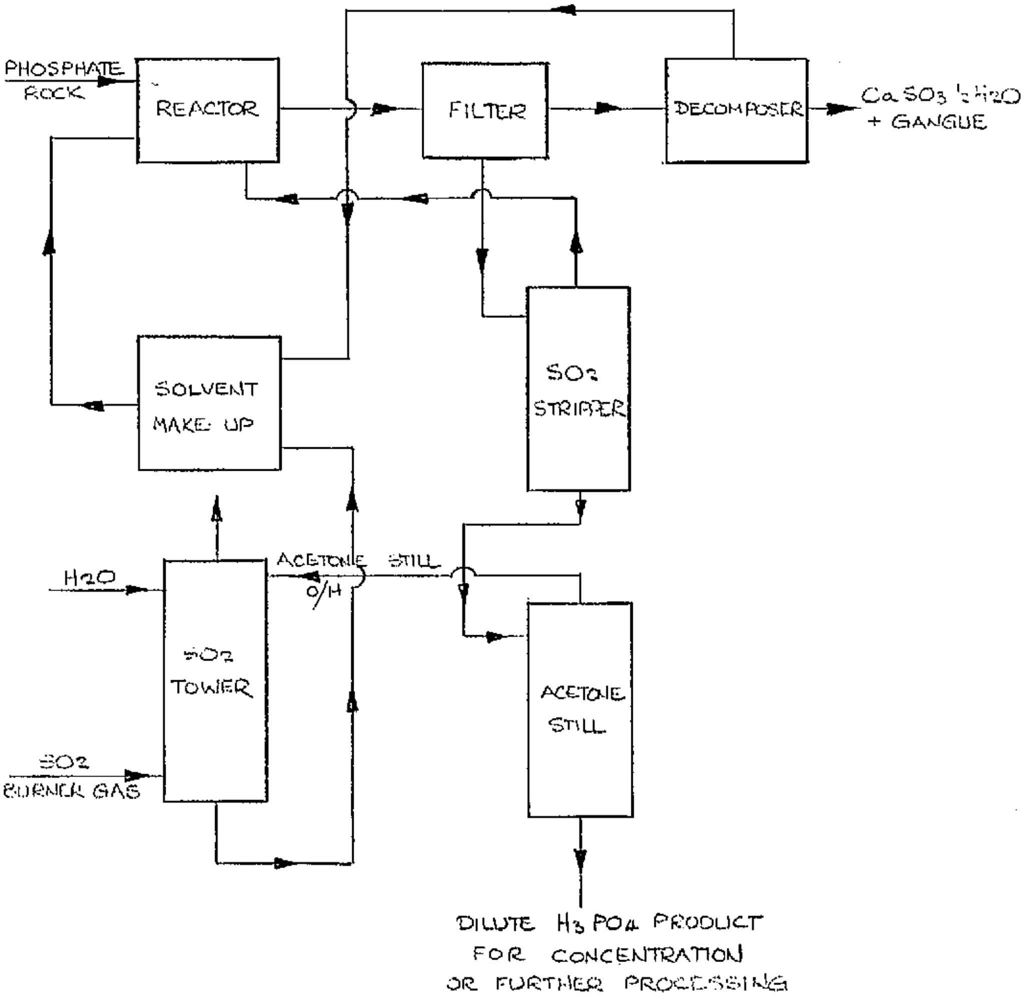


TABLE 9

Heterogeneous Phosphate Process - Direct Stripping

Material Balance
Units Kg/hr

	P_2O_5	CaO	SO_2	Acetone	H_2O
Reactor					
Feed					
Rock	1000	1470	----	----	----
Solvent	----	----	6000	15600	2400
Products					
Solution	950	30	2520	12165	1395
Cake	50	1440	3480	3435	1005
Decomposer					
Feed	50	1440	3480	3435	1005
O/H	----	----	1800	3431	765
Cake	50	1440	1680	4	240
SO_2 Stripper					
Feed	950	30	2520	12165	1395
O/H	----	----	2520	214	2
Acetone Still					
Feed	950	30	----	11951	1393
O/H	----	----	----	11939	31
Product Bottoms	950	30	----	12	1362

TABLE 9 Continued

	P_2O_5	CaO	SO_2	Acetone	H_2O
Recycle & Makeup					
Decomposer O/H	----	----	1800	3431	765
Stripper O/H	----	----	2520	214	2
Acetone Still O/H	----	----	----	11939	31
Total Recycle	----	----	4320	15584	798
Makeup	----	----	1680	16	1602
Sulphur Dioxide Tower					
Acetone Still O/H	----	----	----	11939	31
Water	----	----	----	----	1602
SO_2 18% Burner Gas	----	----	1680	----	----
Solvent Product	----	----	6000	15600	2400

Product 2354 Kg/hr at 40 Wt% P_2O_5 Solution

TABLE 10

Heterogeneous Phosphate Process - Direct Stripping
Energy Balance

Production 2354 Kg/Hr 40 Wt% P_2O_5 - Solution

Process Requirements		K cal/hr
Decomposer	+	1,389,191
SO_2 Stripper	+	749,215
Acetone Still	+	1,741,868
Heat Recovery		
75% Heat of Vaporization	-	2,165,025
Sulphur Burning	-	1,896,720
Nett Input	+	181,471

b. 2-phase System

The process proceeds as follows:

i. the rock is reacted with the solvent, and a solution phase and a solid phase result.
The acetone-SO_2-water solvent stream also carries recycled H_3PO_4.

ii. after filtration the cake is passed to a decomposer, where acetone and SO_2 are recovered by heating to 135°C. The residue is calcium sulphite ·5 H_2O.

Note: The cake need not be washed, because the exchange system would be countercurrent and the cake would be contacted only by in-coming solvent.

iii. the filtrate goes to an SO_2 fortifier, where water and SO_2 are added to bring the solution into the 2-phase region.

Note: There is enough strong SO_2 gas in the overheads from the SO_2 stripper to supply this fortification stage.

iv. the two phases are then separated into water-rich and SO_2-rich streams.

v. the water-rich stream goes to a solvent recovery system, where acetone and excess SO_2 are removed by stripping and distillation.
The result is an aqueous solution of H_3PO_4, which could be from 30-50% P_2O_5 by weight, depending on the parameters of the phase system.

vi. the SO_2-rich phase goes to an SO_2 stripper to reduce SO_2 content.

vii. the overheads of the SO_2 stripper are used partly for the SO_2 fortification stage; the rest goes back to solvent makeup.

Note: Small amounts of acetone will be lost through the system, but the only makeup chemical needed in quantity will be SO_2, to replace the SO_2 that combines with lime to produce calcium sulphite.

viii. the H_3PO_4 can be recovered or used in further reactions.

Following are:

1. Schematic Flowsheet: Figure VII
2. Material Balance: Table 11
3. Energy Balance: Table 12

FIGURE VII

PHOSPHORIC ACID HETEROGENOUS REACTION
2 PHASE SYSTEM

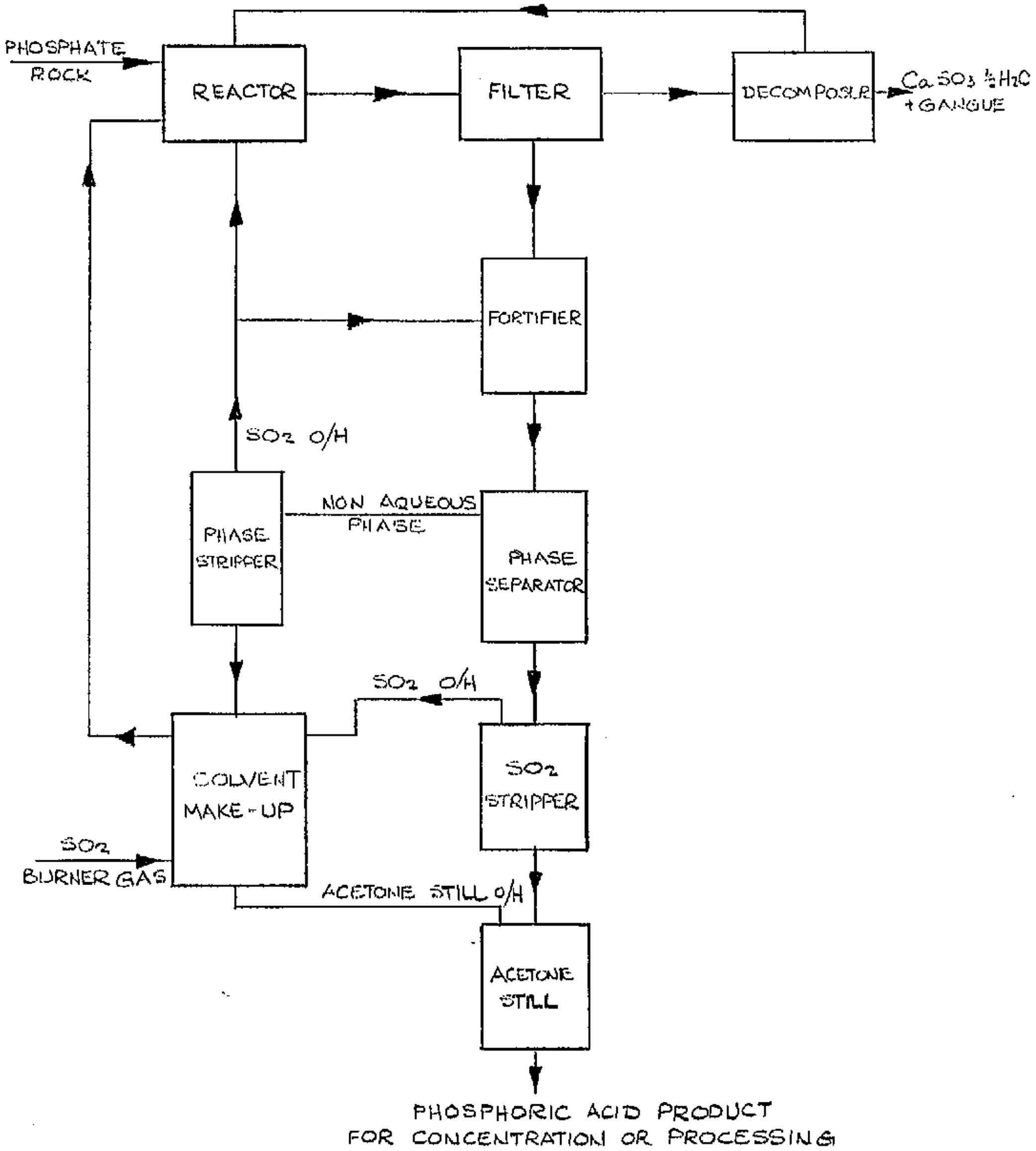


TABLE 11

Heterogeneous Phosphate Process - Two Phase System

Material Balance

Units Kg/hr

	P_2O_5	CaO	SO_2	Acetone	H_2O
Feed					
Rock	1000	1470	----	----	----
Solvent	400	----	6000	15600	2400
Products					
Solution	1350	30	2520	12165	1395
Cake	50	1440	3480	3435	1005
Decomposer					
Feed	50	1440	3480	3435	1005
O/H	----	----	1800	3431	765
Cake	50	1440	1680	4	240

TABLE 11 Continued

	P_2O_5	CaO	SO_2	Acetone	H_2O
Recycle & Makeup					
Decomposer O/H	-----	-----	1800	3431	765
SO_2 Phase	400	-----	6511	10989	1611
Solvent Recovery O/H	-----	-----	362	1174	24
Total Recycle	400	-----	8673	15594	2400
			6000	15600	2400
Makeup	-----	-----	2673	6	-----
SO_2 Phase Stripper					
Feed	400	-----	6511	10989	1611
O/H	-----	-----	6511	194	4
Bottoms	400	-----	-----	10795	1607
SO_2 Fortification					
Stripper O/H	-----	-----	6511	194	4
Feed	-----	-----	4353	-----	-----
Balance to Solvent Makeup	-----	-----	2158	120	3
Feed	1350	30	2520	12165	1395
Makeup	-----	-----	4353	-----	940
Phase Separation					
Feed	1350	30	6873	12165	2335
Water Phase	950	30	362	1176	724
SO_2 Phase	400	-----	6511	10989	1611

TABLE 11 Continued

	P_2O_5	CaO	SO_2	Acetone	H_2O
Solvent Recovery					
Feed	950	30	362	1176	724
O/H	----	----	362	1174	24
Product Bottoms	950	30	----	4	700
Solvent Makeup					
Decomposer O/H	----	----	1800	3431	765
Stripper O/H Balance	----	----	2158	194	3
SO_2 Tower Bottoms	400	----	1680	10795	1607
Solvent Recovery O/H	----	----	362	1174	24
Total Recycle	400	----	4320	15520	2400
Solvent	----	----	6000	15600	2400
Makeup	----	----	1680	----	----
SO_2 Tower					
Feed					
Stripper Bottoms	400	----	----	10795	1607
SO_2 Burner Gas	----	----	1680	----	----
SO_2 Tower Bottoms	400	----	1680	10795	1607

Product 1684 Kg/hr at 56 Wt% P_2O_5 - Solution

TABLE 12

Heterogeneous Phosphate Process - Two Phase System

Energy Balance

Production 1684 Kg/hr 56 Wt% P_2O_5 -

Process Requirements		K cal/hr
Decomposer	+	1,389,191
SO_2 Stripper	+	1,130,448
Solvent Recovery	+	312,418
Heat Recovery		
75% Heat of Vaporization	-	1,401,254
Sulphur Burning	-	1,896,720
Nett Input	-	492,917

4. Hydrochloric Acid Process

The processes for making potassium bisulphite give hydrochloric acid, approximately 4M, as a second product.

Our literature survey revealed that Israel Mining Industries has a process for making phosphoric acid by the acidification of phosphate rock with HCl. It was difficult to obtain details of this process; for example, nowhere was the concentration of HCl used stated explicitly, but we have put together a material balance, which follows as Table 13.

The process proceeds as follows:

a. HCl and phosphate rock are mixed, and phosphorus, lime, and some impurities go into solution.

b. after clarification, the solution goes to a continuous countercurrent reactor, where the H_3PO_4, the free HCl (25% excess was used), and part of the calcium (approximately 4%) are extracted into the solvent phase.

c. the solvent phase is washed with some of the product of the evaporators in the H_3PO_4 concentration system to remove the adventitious calcium.

d. the purified extract is washed with water to return the H_3PO_4 to the aqueous phase.

e. the aqueous phase is then passed to a triple-effect evaporator & emerges as the final product, containing 70% P_2O_5 and 0.5% HCl.

f. the raffinate from the extractors is distilled to recover the 1% of solvent dissolved in it.

g. bottoms can be evaporated further to recover $CaCl_2$.

h. remaining overheads from the evaporator, and recovered solvent from the washing stage, are recycled.

Note: With solvent recovery, but without concentration of the H_3PO_4, the product contains 7% P_2O_5 solution in water.

Following are:

1. Schematic Flowsheet: Figure VIII
2. Material Balance: Table 13
3. Energy Balance: Table 14

FIGURE VIII

HYDROCHLORIC-BASED ROUTE TO PHOSPHORIC ACID

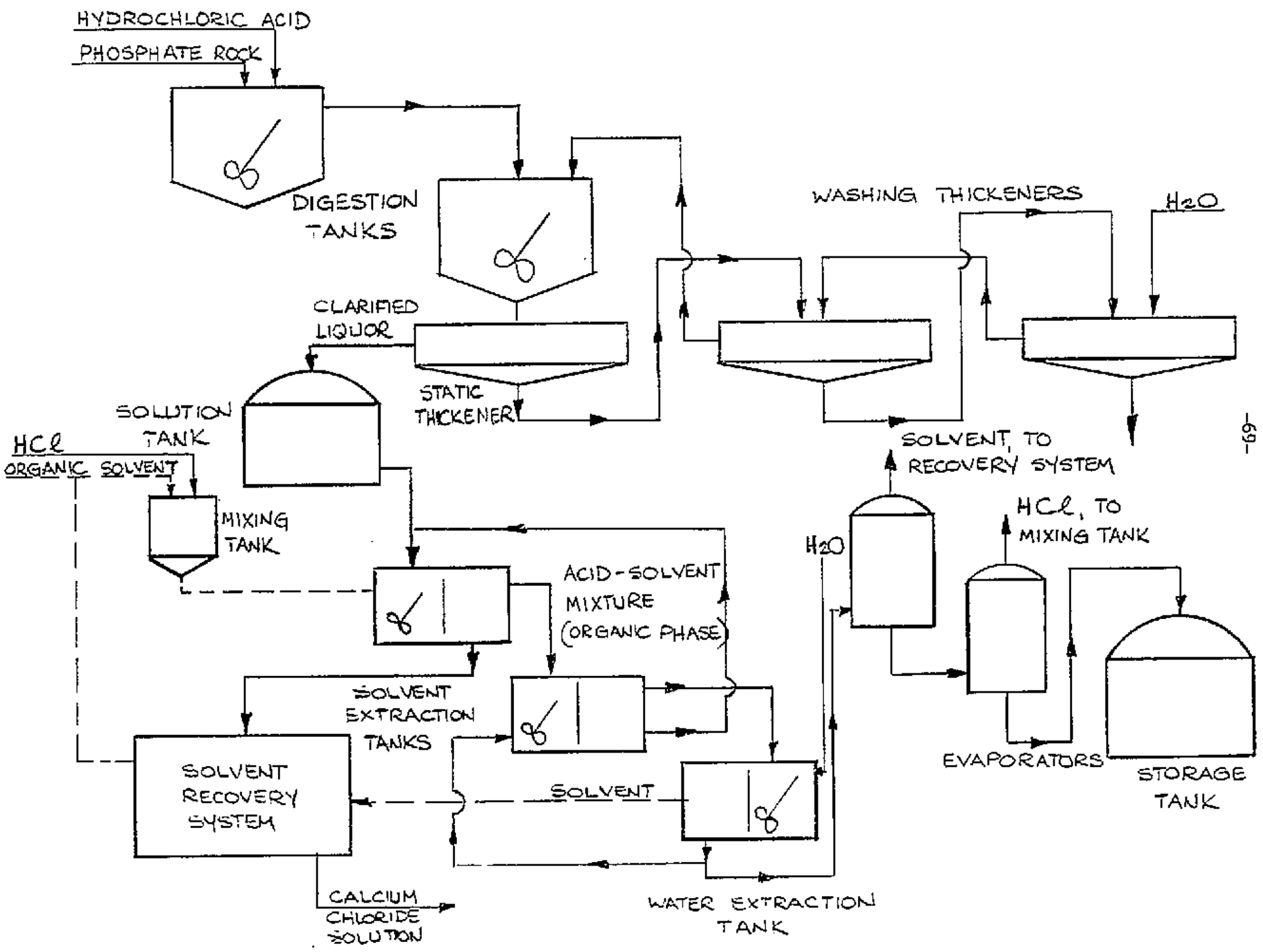


TABLE 13

Phosphoric Acid by HCl Acidification

Material Balance
Units Kg/hr

Note Full data on reagent recycle was not available in the literature consulted and is not detailed in this balance.

	P_2O_5	CaO	HCl	H_2O	$CaCl_2$
Reactor					
Feed	1000	1470	----	----	----
Acid*	----	----	2388	16188	----
Product	1000	----	478	16188	2908

* The makeup acid is assumed to be derived from the potassium bisulphite ion exchange system.

Extraction	P_2O_5	HCl	H_2O	$CaCl_2$	n-butanol
Raffinate	30	120	15700	2790	157
Extract	970	358	488	118	19483

Note The feed, ie. reactor product, is clarified before extraction.

TABLE 13 Continued

Purification

	P_2O_5	HCl	H_2O	$CaCl_2$	N-Butanol
Extract	970	358	488	118	19843
Wash	----	20	1740	----	240
Washed Extract	940	308	488	2	19843
Wash Recycle	30	70	1740	116	240

*Washing

	P_2O_5	HCl	H_2O	$CaCl_2$	N-Butanol
Feed	940	308	488	2	19843
Wash	----	----	13500	----	----
Recovered Acid	900	300	13568	2	407
Recovered Solvent	40	----	420	----	19436

* Back Extraction of H_3PO_4 into a water phase.

H_3PO_4 Concentration

3 Effect Evaporation

	P_2O_5	HCl	H_2O	$CaCl_2$	N-Butanol
Recovered Acid	900	300	13568	2	407
O/H	----	294	13183	----	407
Product	900	6	385	2	----

Solvent Recovery

	P_2O_5	HCl	H_2O	$CaCl_2$	N-Butanol
Raffinate	30	120	15700	2790	157
O/H	----	----	381	----	157
Bottoms	30	120	15319	2790	----

TABLE 13 Continued

Recycled Streams

	P_2O_5	HCl	H_2O	$CaCl_2$	n-Butanol
Solvent Recovery O/H	----	----	381	----	157
Evaporator (Butanol Recovery Only)	----	294	500	----	407
Recovered Solvent	40	----	420	----	19436
Total Recycle	70	314	3041	116	20,000

Product (a) 14040 Kg/hr 6.9 Wt% P_2O_5 solution prior to distillation after Butanol recovery.

(b) 1360 Kg/hr 71.3 Wt% P_2O_5 solution after complete evaporation.

TABLE 14

Phosphoric Acid by HCl Acidification

Energy Balance

Production 900 Kg/hr P_2O_5 70% P_2O_5 - Solution

		K cal/hr
Process Requirements		
Phosphoric Acid Concentration	+	8,233,560
Solvent Recovery	+	1,490,452
Heat Recovery		
75% Heat of Vaporization	-	5,534,922
Nett Heat Input	+	4,189,090

5. Alternative Products

Units Kg/hr

1. Potassium Metabisulphite

Crystallizer/Drier

	K	Na	H_2O	SO_2	Acetone
Feed	514	8	3277	816	1
SO_2	—	—	—	25	—
O/H	—	—	3277	—	1
Bottoms	514	8	—	841	—

Product 1461 Kg/hr $K_2S_2O_3$

2. Potassium Sulphite

Metabisulphite Drier Bottoms

Kiln Feed	514	8	—	841	—
Kiln O/H	—	—	—	410	—
Kiln Bottoms	514	8	—	431	—

Product 953 Kg/hr K_2SO_3

3. Potassium Sulphate

	K	Na	SO_2	SO_3
Oxidiser Feed	514	8	431	---
Air Stoichimetric Requirement			108 Kg/hr	O_2
Oxidiser Bottoms	514	8	---	539

Product 1060 Kg/hr K_2SO_4

4. Mono Potassium Phosphate

Elution of Potassium Charged Resin

	K^+	P_2O_5	SO_2	Acetone	H_2O
Resin Phase	514	---	---	---	---
Elutant	---	933	1311	2811	4069
Eluate	514	933	1311	2811	4069

SO_2 Stripper

	K^+	P_2O_5	SO_2	Acetone	H_2O
Feed	514	933	1311	2811	4069
O/H	---	---	1311	40	10
Bottoms	514	933	---	2771	4059

Acetone Still

	K^+	P_2O_5	SO_2	Acetone	H_2O
O/H	---	---	---	2770	90
Bottoms	514	933	---	1	3969

Crystallizer

	K_2O	P_2O_5	H_2O
Feed	514	933	3969
O/H	---	---	3969
Product	514	933	---

Product 1788 Kg/hr Potassium Monophosphate

PRODUCTS

The great advantage of the processes described in this paper over conventional processes is that they open up possibilities for making a variety of end products from the first compounds that appear, whereas conventional processes make an initial product that is also the end product and cannot be converted readily into further commodities.

Our initial products are potassium bisulphite and phosphoric acid. These are both marketable, but they can also be used as the raw materials for an impressive list of other products. As well, from the preparation of these initial products, two important by-products result: hydrochloric acid and calcium sulphite. (Calcium sulphite is a by-product of the phosphoric acid process).

Another advantage of these versatile systems is that the same equipment as is used to process potassium chloride can be used to process sodium chloride. This makes possible a third initial product, sodium bisulphite, and a long list of sodium end products.

Our first goal is to produce potassium sulphate and potassium monophosphate as end products, but we did a brief telephone survey of pulp and paper mills in New Brunswick, Nova Scotia, and the Gaspé and found that three types of chemicals are used:

1. saltcake (Na_2SO_4), used as makeup in the kraft process.

2. sulphur, used as a source of SO_2 in the sulphite and CTMP mills.

3. caustic or soda ash, also used in the sulphite and CTMP mills.

Saltcake is used in the kraft process as a makeup chemical, because it is a source of both sodium and sulphur. In the recovery system it is reduced to sodium sulphide. Sodium sulphite (Na_2SO_3) would work as well, because in the recovery process it, too, would be reduced to sodium sulphide.

A New Brunswick plant making sodium sulphite from sodium bisulphite, therefore, would provide a local source of supply for the region's kraft mills. At present, saltcake has to be imported into the region from Saskatchewan or from out of the country. 60,000 tons a year are needed, equivalent to 53,000 tons of sodium sulphite.

It would be easy to convert sodium sulphite to the sulphate and provide the mills with the chemical they are used to; but there would be no advantage in this, because sodium sulphite would work as well and could be delivered more cheaply than saltcake. It might even be possible to deliver the product as the saturated solution, obviating the need for evaporation, which would mean lower costs to both manufacturer and buyer.

Sodium bisulphite is used as a cooking chemical in sulphite mills. Elemental sulphur is burned to make SO_2, which is treated with soda ash or sodium hydroxide to form the bisulphite. Our proposed plant could supply a concentrated solution of sodium bisulphite already prepared.

Sulphite mills in the New Brunswick, Nova Scotia, Gaspé region use 62,000 tons of sodium sulphite or bisulphite per year, and Lake Utopia, a neutral sulphite mill, uses about 3,000 tons of sodium sulphite. Total tonnages therefore, are about 62,000 tons of sodium sulphite and 56,000 tons of sodium bisulphite.

Sulphur dioxide could also be recovered without much difficulty and without interfering with the makeup system by using stripper overheads. This would be a nearly pure gas, which would require only the removal of traces of acetone and water before it would be ready for sale. The quantity of SO_2 gas consumed in the region (mainly in New Brunswick) is about 3600 tons per year.

Our survey did not extend into the State of Maine, but there are five kraft mills there within easy hauling distance of Saint John.

Opportunities inherent in these versatile processes are obvious and interesting. The next phase must surely be detailed economic studies of the costs of production and plant costs. No firm cost data are available at present, but it seems likely that sodium chemicals made as proposed here would be cost competitive with those now being made in the mills out of imported ingredients, or with saltcake that has to be hauled long distances.

1. Potassium Bisulphite

Potassium bisulphite is obtained as the initial product of the potassium bisulphite process.

It can be sold either as a solution, after concentration, or as the solid salt, after crystallization. (The solid form is called potassium metabisulphite).

Market Data

Statistics Canada does not cite a Canadian manufacturer of potassium bisulphite.

Canadian Market:

1981 - 278 tonnes
1982 - 102 tonnes (Statistics Canada)

Source: chiefly West Germany.

Today's Price: $400. (Can.)/tonne. (Chemical Marketing Reporter)

2. Potassium Sulphite

Potassium sulphite is prepared by treating potassium bisulphite solution with lime.

Equation:

$$2\ KHSO_3 + Ca(OH)_2 = K_2SO_3 + CaSO_3$$

Alternatively, it can be prepared by heating potassium bisulphite or potassium acetone sulphonate to 135°C.

Equation:

$$KHSO_3 \xrightarrow[135^\circ]{Heat} K_2SO_3 + SO_2$$

After filtering and washing, the product is concentrated, usually to the crystalline stage, for market.

Market Data

Statistics Canada does not cite potassium sulphite either as made in Canada or as imported into the country. The Canadian market, therefore, must be very small.

3. Potassium Sulphate

Potassium sulphate is prepared by the oxidation of potassium sulphite in air.

Oxidation can be accomplished in solution or in a kiln. (The same kiln used to prepare potassium sulphite from potassium bisulphite could be used).

Equation:

$$K_2SO_3 + O_2 \xrightarrow[135^\circ]{Kiln} K_2SO_4$$

Market Data

Statistics Canada data may be incomplete, as they do not cite a Canadian manufacturer.

Canadian Market:

(Statistics Canada cites the imported commodity only).

K_2SO_4 (over 52% K_2O),
1981-3170 tonnes
1982-817 tonnes

K_2SO_4 (less than 52% K_2O, probably fertilizer grade),
1981-18,288 tonnes
1982-20,045 tonnes

Source: chiefly the USA.

U. S. Market:

(Chemical Marketing Reporter, 1981)
US Production Capacity (1981), 1,557,000 tons
Estimates for 1984,

US Market, 1,680,000 tons
Growth, 3%/year
US Exports, 30% of production

Today's Price:

(Chemical Marketing Report)
$145. - 175. (Can.)/tonne
$ 3.10/unit ton (50% K_20 basis)
$193. (Can.)/ton

4. Monopotassium Phosphate

Monopotassium phosphate can be prepared in several ways:

a. by the effect of heat on a mixture of potassium bisulphite and H_3PO_4 in stoichimetric proportion.

Equation:

$$KHSO_3 + H_3PO_4 = KH_2PO_4 + SO_2 + H_20$$

b. evaporation and crystallization would give the desired product. SO_2 would be recovered for recycle.

c. by eluting the ion exchanger, loaded with K^+ ion with the H_3PO_4-P-FS mixture that comes from the filter after calcium and insoluble gangue materials have been removed by ion exchange and filtration.

Equation:

$$KCl + \text{Resin-H} \rightarrow \text{Resin-K} + HCl$$

$$\text{Resin-K} + H_3PO_4 + \text{PF Solvent}$$

$$= \text{Resin } H^+ + KH_2PO_4 + \text{PF Solvent}$$

$$KH_2PO_4 + \text{PF Solvent} \xrightarrow[\text{Heat}]{} KH_2PO_4 + \text{PF Solvent} \uparrow$$

By these operations three important reactions can be achieved:

a. potassium chloride (KCl) can be converted to HCl.
(The exchanger is left in the K^+ mode).

b. monopotassium phosphate can be generated, by eluting the K^+ resin with phosphate rock solution that still contains Ca^{++}

The reactions proceed as follows:

i. a K^+ to Ca^{++} exchange takes place. The eluent contains K^+, H_3PO_4, and the P-F solvent.

This is an alternative to (c) above.

Equation:

$$\text{Resin-K} + CaH_2PO_4 \text{ solution} + \text{PF Solvent} \longrightarrow \text{Resin-Ca} + KH_2PO_4 \text{ Solution} + \text{PF Solvent}$$

ii. the eluent is stripped to recover acetone and SO_2.

iii. the K^+ and H_3PO_4 combine to form potassium monophosphate. This is recovered from solution by crystallization. (The exchanger is left in the Ca^{++} mode).

Equation:

$$KH_2PO_4 \text{ solution} + \text{PF Solvent} \xrightarrow{\text{Heat}} KH_2PO_4 + \text{PF Solvent}\uparrow$$

c. calcium sulphite is recovered and the acetone and SO_2 are recycled after elution with P-F solvent.

The reaction proceed as follows:

i. the Ca^{++} resin is eluted with P-F solvent to return to the H^+ mode.

ii. the eluent is stripped of SO_2 and filtered to recover calcium sulphite.

iii. the filtrate, an aqueous solution of acetone, is returned to chemical makeup for recycle.

Note: It is not necessary to distill the acetone at this point.

Equation:

$$\text{Resin} - \text{Ca} + \text{PF Solvent} \longrightarrow \text{Resin-H} + Ca^{++} + \text{PF Solvent}$$

$$Ca^{++} + \text{PF Solvent} \xrightarrow{\text{Heat}} CaSO_3\downarrow + SO_2\uparrow + \text{acetone} + H_2O$$

All of these reactions could be carried out in a double-loop Higgins Contactor. Experimental trials would be necessary to define conditions.

Market Data

Statistics Canada does not cite a Canadian manufacturer.

Canadian Market:

Statistics Canada cites imports of 150 tonnes/year.

Note: As mentioned in the Kilborn Ltd. study, this is probably the chemical grade material.

The market for fertilizer grade would have to be developed, but there are advantages to the use of monopotassium phosphate:

1. freight; there are no inert ingredients. (At present, muriate of potash and some form of phosphatic fertilizer are mixed).
2. it is a very good fertilizer for use where both phosphorus and potash are required in the absence of chloride.
3. it can also be ammoniated to give a mixed potassium-ammonium-phosphatic fertilizer.
4. Kilborn estimates the price for the product at between $197. U.S. and $278 U.S./tonne

Assays (given in fertilizer industry terms) follows:

The product in fertilizer terms reports as 0.48.32; $N-P_2O_5-K_2O$ respectively.

5. Other Potassium Products

There are other potassium salts, and sodium salts, that are articles of commerce and imported into Canada.

For example:

1. dibasic potassium phosphate, about 500 tonnes/year.

2. tribasic potassium phosphate, about 60 tonnes/year.

3. potassium pyrophosphate, about 110 tonnes/year.

4. other potassium salts, about 600 tonnes/year - (Statistics Canada).

Note: Depending on the method of preparing H_3PO_4, especially if the ion exchange process were used, the H_3PO_4 product would be suitable for feed and food grade and for general chemical uses, and these other products would be additional possibilities, though in minor amounts.

A similar sequence of sodium compounds would also be possible, and would probably be more important as the tonnages would be three or four times larger. Amounts would still be minor, however, probably the whole market for these phosphates (other than for use as fertilizer) could be produced by one ion exchanging module. The concept of manufacturing these other chemicals would have to be studied separately for market viability.

6. Calcium Chloride

In our processes, calcium chloride ($CaCl_2$) can be made by neutralizing calcium sulphite with HCl, if calcium sulphite is produced in the plant; or it can be made by neutralizing limestone ($CaCO_3$) with waste HCl.

The dried solid would contain 78% $CaCl_2$.

Market Data

Canadian market figures are not available.

U. S. Market: (Chemical Marketing Reporter, 1982).

U.S. Production Capacity, 1.4 million tons/year (1982)
U.S. Domestic Demand, estim. 1 million tons (1986)

Plants are located in New York, Michigan, Louisiana, and western states.

Today's Price:

77-80% grade bulk	145.00 U.S./ton
77-80% grade bagged	196.00 U.S./ton

Chemical Marketing Reporter April 30th, 1984.

7. Dicalcium Phosphate

The method of making dicalcium phosphate is the TVA process described earlier.

Market Data

Canadian Market:

1981, 9,000 tonnes
1982, 5,500 tonnes

Today's Price: $634. (Can.)/tonne

Source: the USA

Note: These import amounts are probably food or feed grade.

U.S. Price:

Feed Grade 18½% P 254.00 US/ton

Chemical Marketing Reporter April 30th, 1984

7. Dicalcium Phosphate

The method of making dicalcium phosphate is the TVA process described earlier.

Market Data

Canadian Market:

1981, 9,000 tonnes
1982, 5,500 tonnes

Today's Price: $634. (Can.)/tonne

Source: the USA

Note: These import amounts are probably food or feed grade.

U.S. Price:

Feed Grade 18½% P	254.00 US/ton

Chemical Marketing Reporter April 30th, 1984

DISCUSSION

Six ways of reaching the objectives of this report, the production of fertilizer and other chemicals using acetone-SO_2-water mixtures, have been presented.

The choice of the method to be adopted will depend on several factors, e.g.

1. location of the plant
2. plant costs
3. energy requirements
4. state of the art
5. time requirements - how soon an operating plant is required
6. availability of raw materials

The location of the plant and costs of construction and operation will have to be studied in the next phase of the work.

The decision to proceed and the time to be taken to complete the work are outside the scope of this report.

The state of the art, supply of raw materials, and energy requirements, however, will be briefly discussed in the following remarks, and location will be touched on.

State of the Art

A. Bisulphite Processes

The manufacture of potassium bisulphite (and sodium bisulphite) by

1. the ion exchange process

Pilot units exist, that could be ready for use within weeks.

The manufacturer of the ion exchanger has had wide experience in the field producing commercial size units for various purposes.

The project could therefore enter plant design stage within a short time, probably six months.

Patents: Fraser Cos. Ltd (now Fraser Inc.) patented the use of Pritchard-Fraxon solvents in ion exchange in Canada, the USA, and France. These patents have expired, however, and, as far as we know, have not been renewed.

Only the rights to the Higgins Contactor would have to be considered, therefore, and most of the useful information would be proprietary and would be made available under the terms of a contract to purchase equipment.

2. <u>the heterogeneous process</u>

Most of the relevant work has been done on sodium compounds, not potassium.

None of the work has gone beyond the bench top.

Probably 4 to 6 years would elapse before a plant could be in operation. (This estimate, however, includes all the stages of the project, and the inevitable delays, from arranging funding to starting industrial operations, not just experimental work).

Patents: Fraser patented the heterogeneous process in 1970; therefore they have three more years of protection.

B. Phosphate Processes

1. The manufacture of phosphorus compounds by the TVA Dicalcium Phosphate Process.

This process was studied in extensive bench top work, but would require pilot studies for further development and estimation of plant costs.

Enough data is available from TVA to make pilot studies straightforward.

Patents: TVA holds 1978 U.S. patents.
CSIRO (Australia) has applied for an international patent on their modifications of the process.

2. The Heterogeneous Processes

Phosphoric acid production by heterogeneous reaction has not been patented, and probably is not patentable because of the disclosures made at the Canadian Sulphur Symposium. There is a good deal of proprietary information available, however, to which Fraser Inc. holds title.

The heterogeneous reaction would require a major bench study, because much additional information has become available since it was first studied. The most extensive work has been done at TVA, and their method, which removes some of the calcium before ion exchange begins, is the most efficient so far devised.

3. The Ion Exchange Process

The TVA Method would probably be preferred for an industrial installation unless study of the possibilities of anion exchange turned up something better.

It would be worthwhile to study anion exchange, because it would probably use the equipment more efficiently than cation exchange, as phosphoric acid would exchange as the monobasic form.

If the phosphate system were set up to produce phosphoric acid as the initial product, however, the ion exchange process would be preferred because of the greater purity of the product.

4. The HCl Process

The HCl process does not look very promising when compared with the other ways of achieving the same end, because the H_3PO_4 product is obtained as a rather dilute solution, which means that heat requirements for recovery are likely to be excessive.

This process is also complicated, because there are no easy ways to separate the products. There is no solid phase, so HCl, $CaCl_2$, and the H_3PO_4 have to be extracted, and the complexity of the operation is increased by the carryover, to some extent, of all the components into the various phases.

Solid $CaCl_2$ could be recovered by evaporation, but the costs of making it would be about the same in all the processes.

Raw Materials

The Kilborn study was based on the perceived need to use substantial amount of the sulphuric acid that was to have been generated in the zinc smelter planned for northern New Brunswick. It appears now, however, that no zinc smelter will be built, at least for many years.

The future of New Brunswick industry, therefore, cannot be tied to a zinc smelter. Neither can it be tied, with certainty, to the RPC Sulphating Roast Leach Process, for this process is now only at the beginning of the pilot plant stage, and it will be many years before serious consideration can be given to the construction of a plant.

Exploitation of New Brunswick's potash deposits as the raw material for a potash chemicals industry in the province, therefore, is indefinitely delayed unless another approach can be found, as all the smelter grade SO_2 produced here is committed to the Belledune fertilizer plant.

SO_2 can be made by burning elemental sulphur or pyrite. The pyrite process is fairly expensive and would be difficult to co-ordinate with a progressively developing program of potassium and sodium chemical manufacturing. The burning of elemental sulphur, however, is fairly simple and there is a source of the material in the oil refinery.

The processes presented in this report could use SO_2 derived from burning elemental sulphur and would recycle all that was not bound up in end products. This would maximize the economics of the industry and eliminate the waste SO_2 problem.

This might solve the problem of what to do with waste hydrochloric acid.

Potash, salt, and lime can all be obtained in the area between Nawigewak and Havelock. Only acetone and phosphate rock would have to be imported.

Plant Location and Size

Plant location and size will depend very much on the source of the SO_2 used and the final disposition of the products.

Because there may not be much waste SO_2 available in New Brunswick, at least for many years (all the smelter gas now produced here being already committed to Belledune Fertilizer), the source of SO_2 will probably be elemental sulphur, which is produced in Saint John or can be brought into the province by rail or sea. Saint John appears to be a likely location, therefore, but the delivered price of sulphur would probably be very little lower for the locally produced material, and so plant location need not be dictated by the source of sulphur.

Movement of raw materials and products would be important to plant location.

If potassium sulphate (K_2SO_4) were to be the only product, production (probably 50,000 tonnes/year) would be mostly for export, and shipment by sea would be indicated: the nearer to dockside, therefore, the better the f.o.b. price; for it is cheaper to haul 60% K_20 potash than 50% K_20 K_2SO_4.

If, however, a plant were planned that would also make sodium sulphite and bisulphite, it would probably be best located in Sussex close to the mine, because the product would be hauled around New Brunswick and to the Gaspé, Nova Scotia, and Maine, as well as to shipping points for sea traffic.

Note: It is not the business of this report to consider sodium compounds, but the possibility of making them is so logically a part of the industrial development being investigated, that passing reference to them must be made from time to time.

If phosphoric acid, dicalcium phosphate, and monopotassium phosphate were to be made, a dockside location would be necessary, because the phosphate rock would come by sea, and phosphate rock is 60 to 70% lime and gangue materials.

It is most likely that the technology outlined in this report would be used to make a variety of products; and in that case the location of a plant or plants would depend on what was to be made, where the raw materials were to come from, and where the products were to be marketed. These factors would also affect plant size.

For several reasons, it seems likely that the ion exchange process would be preferred, especially because of the advantages of modular construction.

A potassium sulphate unit can produce 14,000 tonnes of K_2SO_4 per year. A double loop phosphoric acid unit can produce 7800 tonnes of H_3PO_4 per year, or 10,000 tonnes of potassium monophosphate. If single module production could be shown to be economically viable, this could mean a change in the way fertilizers are made and distributed. A small plant, located in Carlton County, for example, could produce the fertilizer requirement of the potato-growing area of New Brunswick; and the fertilizers would be appropriate for a potato-growing area, because they would not contain chloride.

It might be possible, also, having a local plant serving a small area, to deliver and distribute the fertilizer in solution, avoiding the expense of preparing solids.

Note: Of course there would be problems in this. This speculation is meant simply to illustrate some of the interesting possibilities offered by the new technology.

Modular construction also offers the option of beginning with a plant of modest size, thus shortening the risks inherent in the initial stages of an industrial operation, without precluding the possibility of growing into a major complex. Cost analyses have yet to be done, but it seems obvious that it would be much easier to finance the establishment of a small plant (particularly as it would be the first of its kind) than to promote the development of a major installation costing several hundred million dollars. Before a large installation is built, it is usual to spend 10 to 20 million on studies of various kinds to secure the investment; but with modular construction, a small unit could be built and put into operation for that amount, without in any way damaging future development.

The purpose of this study has been to draw a parallel between the kind of installation proposed in the Kilborn study and one based on Pritchard-Fraxon technology, but as the facts have been examined, it has become evident that the proposals in this report represent an entirely new approach, not only technically but also economically.

Selection of Processes

1. Bisulphite

Note: The bisulphite-sulphite stage of production can proceed independently of phosphoric acid production, at least initially, though if potassium monophosphate is to be a product, purchased H_3PO_4 will be needed.

Two processes for making potassium bisulphite are presented: the ion exchange process and the heterogeneous reaction.

Until plant cost data are available, it will not be possible to make a final choice, but technically the choice is clearly ion exchange.

Potassium sulphate (K_2SO_4) is made by converting bisulphite to sulphite and then oxidizing the sulphite to sulphate. Both the ion exchange process and the heterogeneous reaction can achieve this objective: the heterogeneous reaction gives solid acetone-sulphonate, which heat converts to bisulphite or sulphite; ion exchange gives a solution of potassium bisulphite, which evaporation and calcination convert to sulphite.

Ion exchange, however, generates a substantial excess of energy, mainly heat derived from the burning of elemental sulphur, and only small amounts of heat are required for recovery and recirculation of acetone and SO_2. Conversely, the heterogeneous reaction requires a considerable amount of extra heat (in spite of the fact that the product is isolated as a solid early in the reaction) because more acetone is used and it all has to be recovered by distillation in order to separate the acetone from the HCl that is generated in the reaction.

If the reaction is stopped at the bisulphite stage, the ion exchange process produces a surplus of 500,000 K cal; the heterogeneous reaction, on the other hand, needs 700,000 to be added.

If the reaction goes to the sulphite stage, ion exchange is still the more economical of energy, requiring 700,000 K cal/tonne fewer than the heterogeneous reaction.

Also, the ion exchange process is technically much further developed than the heterogeneous reaction. Considerable pilot information exists, and exchangers that could be easily adapted to the purposes of the potash industry are in commercial use. The heterogeneous reaction has been studied only on the bench top.

Finally, the ion exchange process enjoys the advantages of modular construction. Each unit can produce the equivalent of 14,000 tonnes of K_2SO_4 per year, and, therefore, small plants could be set up for perhaps 10 million dollars, which could grow or be improved as demand and experience dictated, thus minimizing the risks of embarking on new technology and obviating the need to find and justify the expenditure of 100 to 200 million dollars all at once.

2. Phosphoric Acid Processes

The TVA process stands aside from the mainstream of this study in that it produces only one product, dicalcium phosphate, and makes no contribution to the utilization of potash. Where a supply of waste SO_2 exists, however, this process can be very useful, because it can produce dicalcium phosphate at an energy cost of about 123,000 K cal/tonne without needing H_2SO_4.

One interesting aspect of the TVA process is that it offers an opportunity to use the ion exchangers in subsequent production of H_3PO_4; and further opportunities along this line may appear when the possibility of making monocalcium phosphate in solution is explored.

The TVA process seems to be a good and relatively straightforward method of making calcium phosphate ($CaHPO_4$). Its advantages have been described by McCullough and Phillips and by the Australians who have used it for the beneficiation of poor grades of phosphate rock that are not amenable to use by the conventional H_2SO_4 process.

The Israel Mining process, that uses waste HCl, was also studied for this report, but it was found to require large amounts of energy and so could not compete with other processes presented here.

Three processes, therefore, remain to be considered: ion exchange and two variants of the heterogeneous reaction in which all the calcium is rejected as insoluble calcium acetone sulphonate. One of these variants is a direct process; the other involves manipulation of the phase rule system to reduce energy costs. Both of these process offer certain advantages, but again the choice seems to be ion exchange.

Of the two variants, the 2-phase process requires the least energy, although energy costs are likely to be somewhat more than reported here, because it is likely that somewhat higher water content in the reacting solution would improve reactivity.

The 2-phase stripping variant and the ion exchange process require about the same energy input, but ion exchange gives only 19% P_2O_5 whereas direct stripping gives 40%. Still, for other reasons which follow, ion exchange seems preferable.

Note: We have not calculated comparative energy costs to the same P_2O_5 content, because the rationale of this study is not to make phosphoric acid but monopotassium phosphate, and we aim to use a combination of processes to best effect.

The ion exchange process (in cation form as presented here) could be implemented soonest, because of the extensive technical information already available. The ion exchange process would make a very pure grade of acid with only traces of metallic ion impurities, which would make it suitable for the manufacture of liquid fertilizer and for concentration to 70% P_2O_5, or better, so-called superphosphoric acid. Also, H_3PO_4 coming from the ion exchanger with SO_2 and acetone still in solution could be combined with potassium bisulphite, and recovery of SO_2 and acetone and crystallization of potassium monophosphate could then proceed as a combined operation. This might not save a great deal of energy, but it would allow the common use of some of the equipment, saving capital costs.

3. Combined Operations

The most efficient way to make potassium monophosphate now appears from the data assembled in this report. KCl is converted to potassium bisulphite, and the bisulphite to potassium monophosphate by ion exchange.

The process proceeds as follows:

a. the KCl is ion exchanged to the H^+ form of the resin.

b. the K^+ ion is then removed from the resin by being contacted with a solution of phosphate rock in acetone-SO_2-water solvent, as in the TVA process. The product is a solution of potassium phosphate in acetone-SO_2-water.

c. acetone and SO_2 are removed.

d. the potassium phosphate is recovered by crystallization.

e. the acetone-SO_2-water solvent returns the system to the H^+ form. As a result, calcium is rejected as calcium sulphite solid.

This approach appears to be both rational and economical. It is also applicable to sodium salts, for which there is at least as much demand as there is for the salts of potassium. Much is already known about industrial uses of the equipment (although this sodium -potassium technology is new) so that implementation is sure and could be started without delay. Finally, it offers the advantages of modular construction and the opportunity to proceed in a modest way toward a complete industrial complex.

IMPLEMENTATION

Having determined that the ion exchange approach is to be preferred in both the potassium and phosphate operations, the question now is what steps should be taken to implement the objective of this work: setting up industrial plants to manufacture potassium and phosphate chemicals.

C/S Associates of Oak Ridge, Tennessee, experts in continuous counter-current ion exchange, have been familiar with the Pritchard-Fraxon Process since the original work was done, and could produce plant data in a very short time.

Eluent makeup, and SO_2 and acetone recycle systems were originally designed by J. F. Pritchard & Co. of Kansas City, Missouri, who also worked up full scale plant design for a chemical recovery process for Great Northern Pulp and Paper Co. at Millinocket, Maine. Most of the Pritchard people who did that work, however, have either retired or left the company, so that, unless full records still exist, it is unlikely that J. F. Pritchard could help much now.

Both of these companies should be approached for assistance, however, and certainly C/S Assoc. will be needed for consultations during all the developmental stages of the industrial growth that can go on here; but there should also be a small pilot plant in New Brunswick to study the manufacturing problems of each new product as it comes on stream, to provide training for plant operators, and to encourage local expertise. This would not encroach on the rights of the U.S. consultants, as their input would always be an important factor in any development.

The conversion of sulphite to sulphate will certainly need small-scale piloting. This need not involve the whole process, as we can always begin with purchased sulphite (K or Na), but we will want to study calcination of the product in a rotary kiln at relatively low temperature in air.

Note: An operating, stainless steel, six inch diameter kiln can be obtained second hand in the U.S.A. for 10 to 20,000 dollars U.S., depending on the length of the chamber. There will be other aspects of the work that we will also need to study, but we are not suggesting that the pilot plant will cost vast amounts of money at any time.

Another consideration should be taken into account when evaluating the need for a pilot plant. We are proposing the manufacture of fertilizers and other chemicals by totally new technology, especially revolutionary in the manufacture of fertilizers in that it may well be possible to establish small plants to supply autonomous areas. This will have worldwide application, and it would be wise for New Brunswick firms of design and construction engineers to establish themselves in the field. We could then be the principal experts in all phases of the technology. There is before us a major opportunity for high technology development.