

ISMA* Technical Conference

Seville, Spain

20-24 November 1972

**In 1982, the name of the International Superphosphate Manufacturers' Associations (ISMA) was changed to International Fertilizer Industry Association (IFA).*

A SHORT DESCRIPTION OF THE IMI PROCESS FOR
CLEANING OF WET PROCESS PHOSPHORIC ACID

By

IMI Institute for Research and Development, Israel

INTRODUCTION.

Until quite recently, only two sources of phosphoric acid were available on the market, namely:

- a) Wet-Process phosphoric acid (WPA) made via the sulphuric route which is the largest and cheapest source, but which is quite impure, containing sulphuric acid, F, Ca, Mg, Fe, Al, etc., organic material in solution and in suspension.
- b) "Thermal" phosphoric acid, with a production cost roughly twice that of the wet process acid but, of course, of a greater purity, which can satisfy even food-grade specifications after a minimal chemical treatment.

There exists, however, a growing market for phosphoric acid of an intermediate grade for:

- a. Liquid fertilizers.
- b. Sodium tri-polyphosphate for detergents.
- c. Feed grade supplements for cattle and poultry.
- d. Industrial uses (metal treatment, etc.).

These products cannot, in general, be justified economically on the basis of thermal phosphoric acid. On the other hand, wet process acid is too impure to be used for their manufacture without preliminary purification. Phosphoric acid of a quality close to that of thermal acid, and certainly suitable for the products referred to above, is being produced via the IMI hydrochloric acid route (ref.1).

This paper describes an industrially-implemented process for the manufacture of phosphoric acid for the above products based on purifying the cheapest available P_2O_5 source, namely wet process acid.

In principle, purification can be achieved either by removing the accompanying impurities from the desired component, in this case phosphoric acid, or by removing the acid from the impurities. For wet process acid, purification by the first method has been based on precipitation reactions: it is obvious, therefore, that an operation of this type can only be undertaken in conjunction with the production of phosphate salts, since at least partial neutralization of the phosphoric acid is required for precipitating the impurities. As regards the second method i.e. separation of the acid from the impurities, only solvent extraction can be considered among the standard unit operations. Several processes have been proposed for purifying wet process acid by solvent extraction; an extensive review is given in Ref. 2. The number of references given indicates the intense interest in the production of a purified phosphoric acid by methods based on solvent extraction.

This paper describes a process, already industrially implemented, for the up-grading of wet process acid, based on solvent extraction technology. The process possesses sufficient flexibility to be tailored to give the optimum economic configuration for the production of acid suitable for liquid fertilizers on the one hand, for animal feed supplements on the other, or a combination of products of different grades of purity.

The Process

The process, known as the IMI Phosphoric Acid Cleaning process, has been described in Refs. 1,3. The process depends on the partial extraction of phosphoric acid from wet process acid using isopropyl ether as solvent; decreases in concentration of two orders of magnitude for cationic impurities, and one order in the case of anions, are obtainable.

The simplest version of the process produces two products, the clean acid and a residual acid containing the balance of the P_2O_5 and the non-extracted impurities. Variations on the basic process, as described below and illustrated in Figure 1, involve additional exploitation of the separation factors between the phosphoric acid and the impurities present in the WPA, treatment of the residual acid, or combinations of both. Cost figures for all variations are given in Table 1; comparative compositions of each type of product are given in Table 2.

It is worth noting that feed wet process acids of widely differing levels of impurities, produced from phosphate rocks of differing origin and quality, can all be cleaned up by this process and all give essentially similar grades of clean products.

Variation 1

This is the simplest variation. It involves extraction of phosphoric acid into the solvent, and its subsequent release, without any additional purifying operations. 60 - 70% of the P_2O_5 entering in the feed acid appears in the product as phosphoric acid containing 50% P_2O_5 of a quality sufficiently high to be used in the compounding of liquid fertilizers. The balance of the P_2O_5 , and the bulk of the impurities, report to the residual acid. If only a portion of the main WPA plant's production is cleaned, the residual acid may be incorporated in the merchant acid product of the main plant. If this is not the case, it may be used to make solid fertilizers e.g. triple superphosphate or an ammoniated NPK blend. This variation has the lowest conversion cost for P_2O_5 and produces the lowest quality of clean acid.

Variation 2

This variation aims at the production of acid suitable for the manufacture of detergent grade sodium phosphates. It is basically similar to Variation 1, with a purifying liquid-liquid contacting step interposed between the extraction and release operations. This step exploits the difference between the distributions of phosphoric acid and the dissolved impurities to give a higher grade of clean acid product. P_2O_5 recovery in the clean product is slightly lower than for Variation 1, and the residual acid is utilized in a similar way.

Variation 3

In situations which do not permit the utilization of the residual acid in the manner suggested in Variation 1, this Variation 3 virtually eliminates the production of residual acid. The main operations are similar to those described in Variation 1 or 2, depending on the degree of purity required. The residual acid produced in the primary extraction is processed in a subsidiary extraction operation whereby an additional quantity of P_2O_5 is separated from the impurities. This additional recovery is incorporated in the main process stream at the appropriate place.

Recoveries as high as 95% of the P_2O_5 in the entering wet process acid stream are attained in this double extraction variation, while approximately five per cent remains as what is essentially a mixture of phosphates of the initially present cationic impurities.

Variation 4

This variation produces a combination of a range of products, varying from solid fertilizer to a phosphoric acid suitable for animal feed supplements. After the basic extraction step, the production line is split into parallel routes. Each of these routes comprises an intermediate purification step, based on liquid-liquid contacting, which is tailored to the degree of purity required in the product. The feed grade line incorporates an intensive purification step, to attain a minimum level of impurities complying with specifications for animal feed supplements. The second line, where the purification step is less stringent, produces detergent grade acid. The effluents from the purification steps of the above two lines are combined to give a liquid fertilizer grade product. Finally, the residual acid is processed to solid fertilizer or may be treated for further P_2O_5 recovery as in Variation 3.

Obviously, the three main products may be produced in widely varying quantities; the costing figures quoted cover production of approximately equal quantities of feed, detergent and liquid fertilizer grades.

Process Technology

The physico-chemical basis of the process (Ref. 1) in which the main process steps are conducted in an invariant system of three phases, makes process control inherently easy, since phase compositions are completely fixed in the presence of all three phases; this fact also permits execution of the main process steps as single-step operations. Optimization of the process from an engineering point of view shows that, in certain cases, advantages are to be gained by operating these steps as two-stage counter-current operations. The process thus has an inherent simplicity which distinguishes it from other solvent extraction processes involving multi-stage operations.

Liquid-liquid contacting operations are carried out in mixer settlers; IMI has extensive experience in the design and operation of this type of equipment (Refs. 4,5). The remaining processing operations are completely conventional.

Corrosion problems are minimized since process conditions are such that most of the equipment can be constructed of inert plastic materials, e.g. rigid PVC, glass fibre-reinforced polyester, etc. Stainless steel alloys and graphite are used for pumps, heat exchanger tubes, agitators, etc.

The use of a volatile solvent postulates that proper precautions be taken in the design of plant and equipment to comply with the relevant safety requirements and to minimize mechanical losses of solvent.

Implementation

The IMI Cleaning process has been implemented by Fertilizantes Fosfatados Mexicanos, who are operating a plant producing detergent grade acid. A further plant, producing 17,500 t.p.y. of P_2O_5 as detergent grade acid is under construction.

REFERENCES.

1. Baniel A. and Blumberg R. Phosphoric Acid (A.V. Slack, ed.) Vol. 1, part II. Marcel Dekker Inc. New York, 1968.
2. Blumberg R. Industrial Extraction of Phosphoric Acid, Solvent Extraction Reviews 1 (1) pp 93-104 (1971).
3. IMI - Institute for Research and Development, Brit. Pat. 1,112,033 (1968)
4. IMI - Institute for Research and Development, Brit. Pat. 1,117,959 (1968).
5. IMI - Institute for Research and Development, Brit. Pat. 1,219,033 (1971).

DISCUSSION

MR. IGAL RAZ (IMI Institute for Research and Development, Israel) : Everybody here is aware of the efforts which have been made over the last few years and which are still continuing in the technology of upgrading wet process phosphoric acid.

In the October issue of Fertilizer Abstracts, I have found several references to up-grading by various companies. Other publications which have appeared in the past demonstrate the deep interest which exists in this technology.

IMI decided some years ago to develop a new upgrading technology, and the following goals were achieved:

1. The product is phosphoric acid and not a salt of phosphoric acid.
2. A simplified and flexible technique.
3. A minimum number of contact stages.
4. Minimal decrease in concentration.
5. High loading factor of the solvent.
6. High selectivity.
7. Stable solvent.
8. The use of the extensive accumulated know-how of IMI in solvent extraction operations.

With respect to the first item mentioned, production of acid and not salt, we know of upgrading technologies which provide an upgraded product but as alkali salt. Such a system of course limits the flexibility of the process and generally binds it to a captive market of STPP.

Why upgrading? Let us consider some of the facts which encouraged a new approach to upgrading:

- A 1,000 tpd wet acid plant is common modern practice and problems associated with product distribution are therefore becoming more pronounced; a diversified market is preferable.
- The increasing demand for liquid fertilizer is higher than the increase in demand for other fertilizers.

- Phosphorous production is generally declining and the price of phosphorous keeps rising.

And another why: why solvent extraction? The answer is simply that it is now realised that solvent extraction is an effective separation technique and it is being applied more and more in the heavy chemical industries.

When speaking of upgrading, there are several degrees and specifications which differ one from another. We at IMI generally use the expression "purification" to describe a higher degree of upgrading, say from wet acid for fertilizer to food grade for Coca-Cola. But there are several intermediate degrees such as liquid fertilizer, detergent phosphates, cattle feed grade phosphates, metal treatment etc., and our cleaning technology can satisfy most of them. And, as a matter of fact, clean acid can even be treated further to reach food grade specifications.

IMI cleaning process is a proven technology which has been implemented on a large commercial scale. The technology is flexible and can be adapted to any wet acid source and provides a wide range of products.

Before ending, allow me to add just two more points. Cleaning provides upgrading of a major part of the wet acid. However, the residual acid holds most of the impurities entering the system and may therefore contain twice as many impurities as there were in the feed, or even more. This acid is used for solid fertilizer. An interesting point in this respect is residual acid from North African wet acid which has been subjected to cleaning. The quality of this residual acid is equivalent to normal Florida wet acid.

My second point is the effect of cleaning on Mg content. Mg is the most disturbing constituent of wet acid when polyammonium phosphates for liquid fertilizer solutions are being considered and many upgrading techniques have been directed to the removal, partially or totally, of Mg. Cleaning provides the reduction of Mg to the ppm level. Thus, for long shelf life liquid fertilizers, a mixture of clean acid with wet acid provides an answer. For Florida wet acid (which is high in Mg) a 50:50 mixture will eliminate the MG problem.

MR. W.R. SCURR (Fedmis, South Africa) : Most of us, I am sure, have been aware for some years that IMI have been practising and developing the use of solvent extraction techniques in the manufacture of phosphoric acid and potassium nitrate. This was started some time ago as a means of separating calcium chloride from phosphoric acid in the IMI process in which phosphate rock is digested with hydrochloric acid.

I am also sure that many of us, myself included, have little or no experience of solvent extraction processes, and have forgotten most of whatever we once knew of the principles involved. As a unit process, solvent extraction just did not seem to have a place in fertilizer technology, but in recent years it, and similar unheard of things like ion exchange, seem to be breaking in on us!

I have looked up the first reference quoted in the paper, and found that the IMI cleaning process described there depends on temperature cycling of the solvent, that is, extraction and separation at a low temperature, followed by heating of the solvent extract and partial separation of the precipitated "clean" acid. The solvent is then re-cooled and returned to the extraction stage.

I should like to ask the author of today's paper whether this procedure is implied in the "acid release" operation? Or is it a complete separation by distillation of the solvent?

I see from the analysis of the acids produced, that the P_2O_5 content of the residual acid is lowered by more than could be expected by the higher concentrations of the impurities. This is presumably by water entering the system. Is this wash water or condensed steam from stripping operations?

Regarding solvent losses, there is a mention of mechanical losses at the end of the paper. I would like to ask whether in addition to these losses it is found necessary to purge the solvent system due to deterioration or build-up of impurities? I am thinking here of organic matter coming in with the feed acid from uncalcined phosphates. If such a purge is in fact necessary in some cases, does this present a disposal problem?

The construction materials listed do not include rubber and rubberlined steel. This is no doubt due to the denaturing effect of the solvent. The product acids and the residual acid must however contain traces of unrecovered solvent, and I wonder whether the same restriction on the use of rubber would apply to the handling and storage equipment for these acids in downstream processes?

My next comment concerns the relative quantities of the various grades of purified acid produced. It is stated that the cleaned acids can be produced in widely varying quantities: this presupposes that you have economic outlets for the residual products in varying quantities and qualities, and that you have

installed the necessary plant to "play all the tunes", which would be expensive while not fully utilized. The obvious application is the case of a solid fertilizer manufacturer who wishes to produce a portion of his wet process phosphoric acid production in one or more of the purer forms and who is then in a good position to absorb the residual acids.

The simplest likely situation would be a basically solid fertilizer manufacturer producing some acid for liquid fertilizers, i.e. Variation 1. For no additional fixed cost, he can practise Variation 2, and produce detergent grade acid instead of liquid fertilizer grade. However, if he wishes to produce a portion of feed grade acid, the fixed cost increases drastically. Have I interpreted the cost table and block diagram correctly? As I understand it, in Variation 2, the addition of the normal purification step (P_1) involves no increase in fixed capital investment, whereas in Variation 4, the addition of P_1 plus P_2 increases the investment cost by some two million dollars.

In many beneficiation processes, it is true to say "the higher the recovery, the lower the purity". This leads me to ask whether the purity of the products is completely independent of the quantity produced. For instance, if only a relatively small quantity, say less than 20% of the input, were required as feed grade acids, with no other products, would this be possible with basically variations 1 and 2 only?

My last point is slightly off the subject. I would have thought that the detergent grade analysis given in the paper would be quite suitable for animal feed production, except possibly for the arsenic content which is not given. If one started with an arsenic-free acid, I think the cost of the extra purification step could be avoided for this purpose.

MR. RAZ : (1) The acid release operation (or stripping the acid from the solvent phase back to the aqueous phase) is achieved by adding water to the loaded solvent. This is a three phase equilibrium operation (free solvent, loaded solvent and aqueous acid). The process water used for the release is supplied mainly from outside. However all water condensates which are free from impurities could be used as well.

(2) Organic matter entering the cleaning system with the feed, originates either from the phosphate rock or from the anti-foam products used in the production of wet acid (such as derivatives of oleic acid). It may tend to accumulate in the solvent and could in due time introduce undesired process

difficulties. However, since the solvent is volatile (62°C - 95% w/w azeotrope), this can be controlled easily by continuous distillation of a small part of the solvent. The rate of regeneration is determined by the level of organics in the feed.

(3) Hard rubber (ebonite) could be used as the construction material for the H_3PO_4 - solvent system. However since hard rubber may differ in specification from one manufacturer to another, representative samples should be tested in each case.

The occurrence at the level of ppm of traces of of unrecovered solvent in the final product acid does not restrict the use of conventional materials of construction for the handling and storage equipment in downstream processes.

(4) The cleaning process is inherently flexible and therefore it is quite natural that one would like to get a plant which can "play all the tunes". But this is, after all, a matter of cost. Generally, one designs the plant according to well defined terms of reference, but one leaves it enough operational flexibility.

(5) The term feed grade was unfortunately mixed up at our end. Originally this grade was defined as "deep clean", which was intended to mean a rather more intensive backwashing which reduces cationic impurities to a level acceptable in food grade acid. Furthermore, we have included in the cost a post-treatment aiming at the production of chemically pure acid.

Acid of "Feed grade" quality can be identified within the specification of detergent grade.

(6) The difference between variation (1) - i.e. production of liquid fertilizer and variation (2) - i.e. detergent grade, lies in the ultimate output: 97,500 tpa versus 90,000 tpa.

(7) The basic cleaning process yields a 60% recovery of P_2O_5 from 53 - 55% P_2O_5 merchant grade acid.

This recovery is strongly dependent on:

- the WPA concentration; for example, only 40% recovery can be achieved with a 50% WPA by the standard process;
- the temperature of extraction; for example, the recovery drop to 50% when the extraction is performed at $30 - 40^{\circ}\text{C}$.

- the degree of backwashing; for example, "deep cleaning" requires larger backwash, which consequently reduces the recovery to 45-50%.

So, aiming at a lower recovery (i.e. 20%) will not significantly simplify the process nor bring about the production of a super pure product. When such matters are considered, the following points should be borne in mind:

- 20% yield necessitates the circulation of 5 ton P_2O_5 per 1 ton P_2O_5 in product. So a 500 tpd WPA train can yield only 100 tpd clean P_2O_5 .
- 20% yield will result in a 4 ton residual P_2O_5 instead of 0.67 ton per 1 ton P_2O_5 .

TABLE 1

Cost Comparison of Variations of the IMI Cleaning ProcessBasis: 150,000 tpy P₂O₅ in feed as 54% P₂O₅ WPA

Variation	1	2	3	
Clean acid product	97,500 tpy P ₂ O ₅	90,000 tpy P ₂ O ₅	143,000 tpy P ₂ O ₅	Detergent acid 36,600 P ₂ O ₅ Feed supplement 36,000 tpy P ₂ O ₅ Liquid fertiliz 29,200 tpy P ₂ O ₅
Residual byproduct	52,500 tpy P ₂ O ₅	60,000 tpy P ₂ O ₅	7,000 tpy P ₂ O ₅	47,600 tpy P ₂ O ₅
Estimated FCI \$ (Battery limits)	2,650,000	2,650,000	4,300,000	4,800,000
Operating costs, \$/ton P ₂ O ₅				
Variable costs	2.10	2.30	5.70	<u>Detergent</u> 2.00
Fixed costs	5.70	6.20	6.00	8.80
Total	<u>7.80</u>	<u>8.50</u>	11.70	<u>10.80</u>

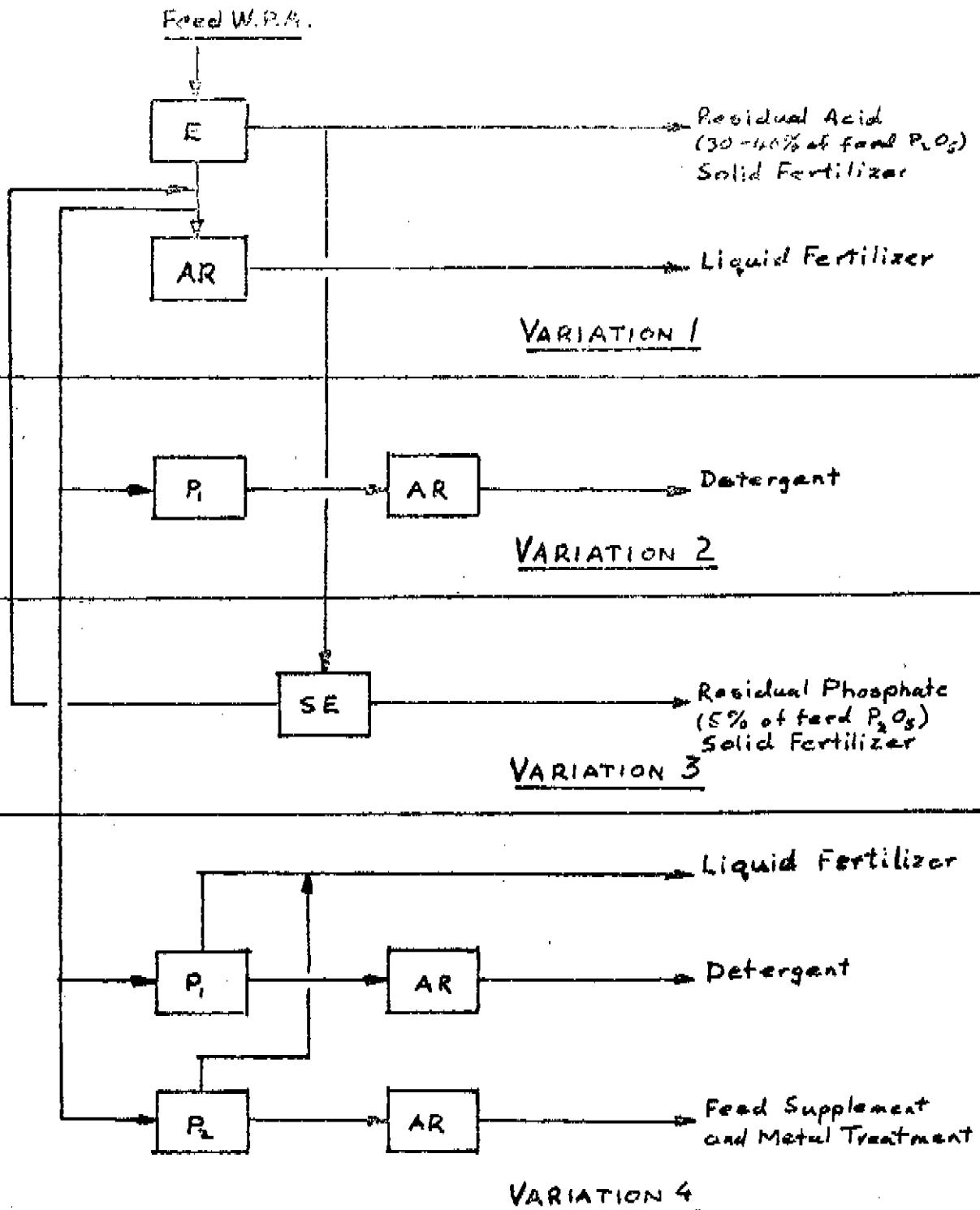
- Notes: 1. Cost of WPA is not included.
 2. Cost of possible treatment of residual product is not included; all costs are loaded to the clean product.
 3. In the fixed costs, capital charges are based on 5% maintenance, 6.7% depreciation and insurance only.

TABLE 2

Product QualityConcentrations in wt. % except where otherwise stated

Component	Feed Acid	Residual Acid	Liquid Fertilizer	<u>Product Detergent</u>	Animal Feed
P ₂ O ₅	50-55	40-47	50	50	50
SO ₄ ²⁻	1.5-6.5	2.0-8.0	1.0-2.0	0.2-0.5	0.2-0.5
FE ³⁺	0.2-0.9	0.4-2.0	0.03	0.003	5 ppm
Al ³⁺	0.1-0.9	0.2-2.0	0.01	0.001	5 ppm
Ca ²⁺	0.1-1.0	0.3-1.5	0.03	0.001	2 ppm
F ⁻	0.1-1.2	0.2-2.5	0.05	0.05	0.05
Mg ²⁺	0.5-0.9	1.0-1.5	0.02	0.001	2 ppm
Cr ³⁺	0.02	0.04	0.001		0.5 ppm
SiO ₂	0.2	0.4	0.03		0.004
As	2-10 ppm	5-15 ppm	2-8 ppm		1 ppm

Fig. 1 - Process Block Diagram



Legend: E - Extraction
 AR - Acid Release
 P_1 - Normal Purification
 P_2 - Intensive Purification
 SE - Subsidiary Extraction