International Fertilizer Industry Association

ISMA* Technical Meetings

Cambridge, United Kingdom
15-17 September 1953

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

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TECHNICAL MEETINGS 1953
Paper (c) 3

September 1953

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CORROSION PROBLEMS IN THE MANUFACTURE OF PHOSPHORIC ACID.

By J.J. Porter and G.C. Lowrison of Fisons Ltd., Felixstowe.

Wet Process Phosphoric Acid is produced from Sulphuric Acid and Phosphate Rock. Thus it contains in addition to Phosphoric Acid, Sulphuric Acid, Hydrofluosilicic Acid, Hydrofluoric Acid, traces of Hydrochloric Acid and abrasive silica and Gypsum. It also contains metallic salts such as Sodium Silicofluoride and Calcium Sulphate which have respectively, steep positive and inverted solubility curves and therefore give rise to scaling difficulties.

The Wet Process of manufacture of Phosphoric Acid may be considered to take place in three stages:- Reaction, filtration and evaporation. In the reaction stage, Phosphate Rock, which consists essentially of fluo apatite ($Ca_5 (PO_4)_3 F$), is fed with Sulphuric Acid into a series of agitated reaction tanks, the contents of which cascade one into the other. The greater part of the slurry is returned to the early stages of the reaction system and the remainder is filtered. The washings from the filter stage are returned to the reaction system.

The mechanism of the reaction is probably for the Phosphate Rock to dissolve in the return slurry and the Phosphoric Acid in the washings to form mainly monocalcium phosphate:-

$$Ca_5 (PO_4)_3F + 7H_3PO_4 = 5Ca (H_2PO_4)_2 + HF$$

The monocalcium phosphate then reacts with Sulphuric Acid to form Phosphoric Acid, and, depending upon the temperature and concentration of the acids, Gypsum, hemihydrate or anhydrite. Most processes aim to produce Gypsum.

$$Ca (H_2PO_4)_2 + H_2SO_4 + 2H_2O = CaSO_4 2H_2O + 2H_3PO_4$$

The hydrofluoric acid reacts with silica contained in the rock to form silicon tetrafluoride, hydrofluosilicic acid and possibly fluophosphoric acids. Phosphoric Acid containing approximately 32% P_2O_5 is produced by this process; but for the manufacture of Dorr Process Triple Superphosphate, acid of concentration 38% P_2O_5 is desirable; this is produced from the process acid by evaporation.

The media for each stage of the process are as follows, each being at a temperature in the range 50 - 80°C.

Raw Materials	Phosphate Rock	Dry abrasive about 70/80% BSS
	Sulphuric Acid	78/94% Cold
Reaction	Liquor	1 part solution containing 32% P_2O_5, 3% H_2SO_4, 1.5% F and 0.67 parts of Gypsum.
	Gas	Air with traces of HF and SiF_4
Filtration	Filtrate	32% P_2O_5 3% H_2SO_4 1.5% F
	1st Washing	22% P_2O_5 2% H_2SO_4 1.8% F
	2nd Washing	5% P_2O_5 0.75% H_2SO_4 1.2% F
Evaporation	Liquid	A typical analysis is: 38% P_2O_5, 2/3% H_2SO_4, 0.2% CaO, 0.4% MgO, 0.3% Fe_2O_3, 0.3% Al_2O_3, 0.8% SiO_2, 1/1.5% F
	Scale	A typical analysis is: 55% F, 10% CaO, 5% SiO_2, 10% P_2O_5

Fig.1 illustrates the suitability of various materials for the various constituents of the above media according to published and recognised data. A substance which is resistant to all the constituents is usually resistant to the mixture although the converse is not true and in this connection lead will be quoted later.

Metals

With the exception of high molybdenum (15/20%) nickel chrome alloys, we have not found any material which will withstand all conditions, although manufacturers claim that alloys of the composition - C .07%, Cr19/22%, Ni28/30%, Si 1.5%, Mo2-2.5%, and Cu 3-3.5%, and certain aluminium bronzes, are also highly resistant.

Two grades of lower molybdenum steel are fairly well available as plate, rod and castings in Europe, of the following composition:-

	316	317
Ni	10/14%	11/14%
Cr.	18.0%	18.0%
Mo	2/2.5%	3/3.5%
C	0.08	0.08

317 is far superior to 316 in its resistance to wet process phosphoric acid, but unfortunately has been in short supply in England of recent years; 316 has been available in its place with a life about half that of 317.

The carbon content is of exceptional importance and should be as low as possible. It should be emphasised that stabilisation with either titanium or columbium presents no remedy for high carbon content. Steels having excessive carbon content lose all metallic characteristics, losing ring, ductility and may even show a flexibility akin to rubber. The parent ingot while possibly of low carbon may produce unsatisfactory castings if foundry technique is faulty.

Wrought material is in general more resistant than the castings, probably because there is less chance of additional carbon being picked up in the foundry, and it is the general experience that castings from the same foundry may be extremely variable.

Hot soaking of the castings is practised in America and on the Continent, but we have not found foundries in this country in favour of adopting this technique.

Extra low carbon steels (ELC.03% C Max.) are now available in America and are generally recommended, but to our knowledge, apart from some experimental pourings, are not available in this country.

Apparatus fabricated from sheet should be welded with a rod having a higher molybdenum content than the parent metal, and provided welding technique is good, no weld decay should result. Special attention should be paid to avoiding sheet bends or producing stresses in the metal in any way whatever. Pieces to be held in a vice or lathe chuck should not be ever tightened or rapid corrosion will result at the point of compression.

All welds should be well brushed to remove scale and if possible dipped for the presence of any foreign matter on the surface will provide points of local corrosion. It is also of importance to remove any painted marks from the surface of the steel or it will be found that the locality will become deeply etched.

Despite their high initial cost, the use of high molybdenum alloys for castings is definitely well warranted. An alloy we have found highly satisfactory has the composition:-

Ni 56%, Cr 15%., Mo 17%, W 5.0%, Fe 5.0%, Mn 0.75%, Si 0.75%.

Peculiarly enough such are more readily available than the 2-4% Mo alloys and foundry technique in the preparation of high molybdenum steel castings has reached a point where the fullest confidence can be placed in the products.

Generally speaking, and considering the availability of material, 317 plate and section in high molybdenum steel castings provide a highly satisfactory solution for most problems.

Lead.

Although lead is attacked by fluosilicic acid, in the presence of Sulphuric Acid, in these concentrations it has been found quite resistant probably due to the formation of a protective sulphate film.

Both type A and B are satisfactorily resistant to acid up to 38% strength, but beyond this we have reason to be dubious of its suitability. With 6% antimony large castings for evaporator bodies have been produced and show a good life with reasonable mechanical strength.

This metal, however, is not suitable for direct contact with mobile gypsum slurry owing to its rapid erosion.

Other Mineral Substances.

Of the other mineral substances, graphite and sulphur cement (55/70% sulphur 30/45% carbon and 0.5/5% of a plasticiser such as Thiokol) are the only ones to stay the field. Graphite when pressed into bricks or tiles is also resistant to abrasion. Sulphur cement has a temperature limitation of 200°F. Asphalt is sometimes used to protect wooden launder covers.

Silicious materials are of course rapidly attacked by the fluorine present in the acid, the life of an evaporator sight glass is only about 250 hours. So called phosphate glass (mainly aluminium metaphosphate) however, is claimed to be resistant to attack, a fact confirmed by small pieces being tested but no opportunity has yet been takan to use a full sized piece.

It is regrettable that the quality of sintered obsidian bricks has deteriorated of recent years as previously these exhibited a fair life.

Silicate base cements (sodium silicate filled with quartz) may be used as a mortar and have a fair life provided temperatures are not excessive and there is not an excessive evolution of fluorine.

Wood.

Certain woods are quite resistant, though again they are not recommended for continual immersion in liquor except of low concentrations.

Rubber.

Both natural rubber and neoprene are resistant to wet process acid up to 50% P_2O_5, provided suitable fillers, such as carbon black, are employed.

While most rubber fabricators prefer to supply hard rubbers, or an outer layer of soft rubber on hard rubber, the user will generally prefer the complete lining to be in soft rubber. Due to the rigidity of a hard rubber lining it is difficult to detect poor adhesion, until the covered part has been in operation for some time, when poor adhesion will make itself apparent by the development of blisters.

The blister cannot be cut away and the lining repaired in a satisfactory manner. Poor adhesion in the case of soft rubber can readily be detected before use and repairs of blisters easily carried out.

Soft rubber is remarkably resistant to abrasion and can be used for slurry pump cases with confidence. Pump impellers of the totally enclosed type are not readily covered, but open impellers are quite satisfactory.

Pure soft rubber, readily available in sheet form is a most useful material for covering slurry boxes and using as seals, but cannot be used at temperatures above 65°C. Such rubber is quickly perished by hydrocarbons, in fact the normal froth from phosphate rock will cause its rapid deterioration.

Pumps are manufactured from this material with fully closed impellers built up from sheets in laminated form which are satisfactory for waste liquor containing weak acid and abrasive solids.

An important feature of rubber covered equipment such as a tank, is that the continuity of the lining can be readily tested by means of a high voltage spark apparatus, the smallest pinhole being easily detected.

It may be necessary for some purposes to lubricate rubber and for this purpose, care must be taken that a lubricant is selected which will not hydrolyse in the presence of acid. For example, potash soap is quite satisfactory if in contact with water, but in the presence of acid, fatty acids are produced which degenerate the rubber. Under certain conditions cursor base greases are satisfactory, but the rubber suppliers are not happy in this respect and do not recommend their use. Silicone greases are stated to be satisfactory but the price makes their use appear expensive.

Special attention should be paid to the design of items intended for rubber covering, and in particular, care should be taken to avoid sharp bends.

After a slow start, site lining of equipment is now as common as lead lining, but the rubber manufacturers, with one or two exceptions, have not been very progressive in this matter.

Rubber latex is used as a basis for acid resisting cement in which it is incorporated with an inert filler and usually some sodium silicate. We have found this very effective as a cement in our effluent flumes which carry very dilute fluoric acids and traces of silica gel.

Provided temperatures below 80°C are employed, and there is no contamination from oil, rubber constitutes one of the most attractive materials available.

Wool.

Of the textiles wool has been found to be resistant, but it suffers from the disadvantage of changing shape and of absorbing large quantities of liquid which if it is water may be returned to the system and cause unwanted dilution.

Synthetic Resins.

Synthetic resins have a wide field of application in this combination of acid substances.

Of the thermo setting resins, phenolformaldehyde applied as a solution and subsequently dried and baked has been found to be very satisfactory in its resistance to fluorine bearing gases; the resin is also believed to be satisfactory as a cement for carbon bricks when used with a carbon filler and it or a similar resin is used for rendering graphite impervious. There is evidence that furfural and cashew nut shell resins with a carbon filler are also satisfactory as cements. It is believed that the flakiness of the graphite filler has an important bearing on the adhesion of the cement to steel. Those cements can be used up to 350°F.

The thermo plastic resins obviously have a severe temperature limitation, but as we usually work at below 90°C, we have found them very useful.

Of the vinyl and vinylidene polymers, we have found saran (polyvinylidene chloride) and orlon (polymer of vinylchloride and and acrylnitrile) valuable as fibres.

Nylon is not satisfactory.

Of the alkyd resins, terylene (polymer of ethyleneglycol and terephthalic acid) is also satisfactory as a fibre.

Of the arylic resins, we have found that perspex (polymethyl methacrylate) is attacked by our phosphoric acid so as to render it less transparent, but it is not destroyed and can be used to protect (glass) sight glasses.

The polymerised ethylenes are very satisfactory. Polythene is not attacked and although we have no experience of it teflon (polymerised tetra fluoroethylene) is almost certainly unaffected by our acid. An added advantage of these resins is that substances will not adhere to them and thus scales do not form very readily.

The polyester styrenes also appear to be satisfactory though we have no experience of them.

MATERIALS OF CONSTRUCTION USED IN THE PROCESS

Raw Material Handling.

Sulphuric Acid. Storage tanks and feeders in mild steel, covers which are subject only to splashing, preferably in lead. Pumps in cast iron or silicon iron, but this latter material being extremely brittle suffers more from mechanical failure than from corrosion. Pipe lines in mild steel with asbestos gaskets.

Phosphate Rock. This presents no particular difficulty but it is advisable to give some protection either in lead or rubber at the actual point of entry of the rock to the reaction system.

Reaction System

Agitator Tanks. The tank shell may be of mild steel plate, or basket construction or wood, but the lining must be capable of withstanding both the conditions of erosion and corrosion. If lead is used as a protective lining it must be well secured by straps to the shell and ample weep holes provided. Lead will not withstand the abrasive effects of Gypsum, some further protection in the form of a tile lining must be provided. Well burnt sintered silica tile may be used to protect the lead but such bricks should be of the best quality and burned throughout. Carbon bricks while four times the initial cost of silica bricks, are well worth the extra expense as their life appears to be limitless. While silicate cements are satisfactory for binding both types of bricks, the additional cost of a phenolformaldehyde, furfural or cashew nutshell resin cement may be well warranted, but its use calls for specialist bricklayers.

Rubber lining of a steel shell has proved satisfactory, but it is advisable to pay attention to the shell design, if this material is to be used. Rounded curbs and top rims should be used. Present day technique permits site lining with air curing rubber to be successfully used. Weep holes are neither necessary nor advisable.

It has been found possible to dispense with the greater part of protection by tile when rubber is used but it is advisable to protect the tank bottom and lower section against damage by shovels when tanks are being cleaned out.

If it is decided to brick line a steel tank it is necessary to provide a membrane either of rubber or of resin cement to take up changes of shape arising thermally or from mechanical vibration.

Agitator Impellers. Most plants now use impellers of simple design running at 400/600 r.p.m. and fixed to suspended shafts. Impellers fabricated from 317 steel plate with shafts of the same material have proved fairly satisfactory. Rubber covering, while satisfactory up to a point has not proved too successful owing to the unavoidable presence of large lumps of scale detached from the tank lining which puncture the rubber; cast impellers have not proved too successful for reasons which will be discussed later; the fabricated impellers while being much lighter are better balanced.

Pumps. Glandless pumps for circulation of slurries and liquids have now been generally adopted. While graphite pumps with mechanical seals are satisfactory for liquor service, rubber lined cases with special steel impeller are adopted for slurry service. 317 steel has a reasonable life but is subject to failure on account of bad foundry technique. The high molybdenum alloys are the most satisfactory found to date and well warrant the high cost. This is illustrated in Fig.2 which, while showing percentage weight loss, can be read as relative penetration. We cannot explain the anomalous relative position of the 2" and 4" impellers though they are confirmed by more than one pair.

Pipe Lines. Lead pipework is now almost completely replaced with rubber or polythene lined pipe or flexible rubber hose. Suitable coupling systems permit stock lengths of R.L. pipe to be kept in stock, cut and assembled as required, as shown in Fig. 3. Polythene exhibits the attractive characteristic of being "scale resistant" but requires careful support.

A good stock of pressure hose with suitable flanged adaptors is a most useful item to have against sudden replacements, while sections of flexible hose at suitable points facilitate dismantling.

Valves. Straight through valves are a necessity in a phosphoric acid plant where the quick scaling characteristics of the liquors in service preclude the use of plug valves. Pinch valves of simple design with an adaptation of the well-known diaphragm valves are generally employed.

Filtration System The design of filters for phosphoric acid plants merits a paper of its own, and we do not intend to enter into a discussion on this point.

If belt filters are employed the maximum amount of rubber covering may be and is, employed, while with table filters the designers favour the use of acid resisting steel.

Rubber belts should be designed so that there is no possibility of the fabric insertion coming in contact with the acid and very great care in manufacture needs to be taken to ensure that when the filtrate passages are cut they do not pierce the fabric. 317 steel has been successfully used for the suction box cover, the box itself being lined with soft rubber with a graphite tile at the point where the strong acid jets through the filtrate passage.

Filtrate receivers which in the past have been generally homogeneously lined with regulus (6% antimony) are now being successfully rubber lined, but such work is best carried out by steam vulcanisation

Contrary to usual belief, the diaphragm valve can be successfully employed for vacuum service.

If adequate spray arresters are provided in the vacuum lines, no special materials of construction are called for in the vacuum pumps, if these are of the wet rotary type, but reciprocating pumps appreciate a condenser in the line, more with a view to removing scale forming gases than to boost up vacuum.

Table filters mostly have 317 steel boxes with valves cast in this alloy or high molybdenum alloy. Wear plates have been made in graphite or hard rubber.

The choice of a filter cloth calls for many points to be examined. It must be chemically resistant and mechanically sound, with a weave close enough to give a reasonably clear filtrate and not subject to sulphate incrustation. Wool cloth has a reasonable life and gives good filtrates but suffers badly from incrustation; the large water retention of these cloths makes them unsuitable for belt filters but satisfactory for table filters where a portion of the cycle may be used for cloth drying. Staple woven plastic cloths are again unsuitable for belt filters, not only due to high water retention but due to excessive stretch, but they are satisfactory on table filters. Monofilament plastic cloth in saran or polythene is the most suitable for belt filters, having little stretch and little water retention. Filtrate clarity is poor with monofilament cloths. Rapid development in plastic cloths makes the question of these cloths extremely open.

Evaporation. There is probably more variation in this section of the phosphoric acid plant than in any other. Extremely corrosive and scale forming liquor is being treated and makes the solution of the problem one of great importance.

Tower evaporators using hot gases are constructed in graphite bricks, with or without a backing of lead.

Submerged flame evaporators have been employed, having tile lined tanks with a backing of rubber, the burners being of 317 or high molybdenum alloy. A very severe fume problem together with the use of expensive fuel has more or less ruled these evaporators out of use in Europe.

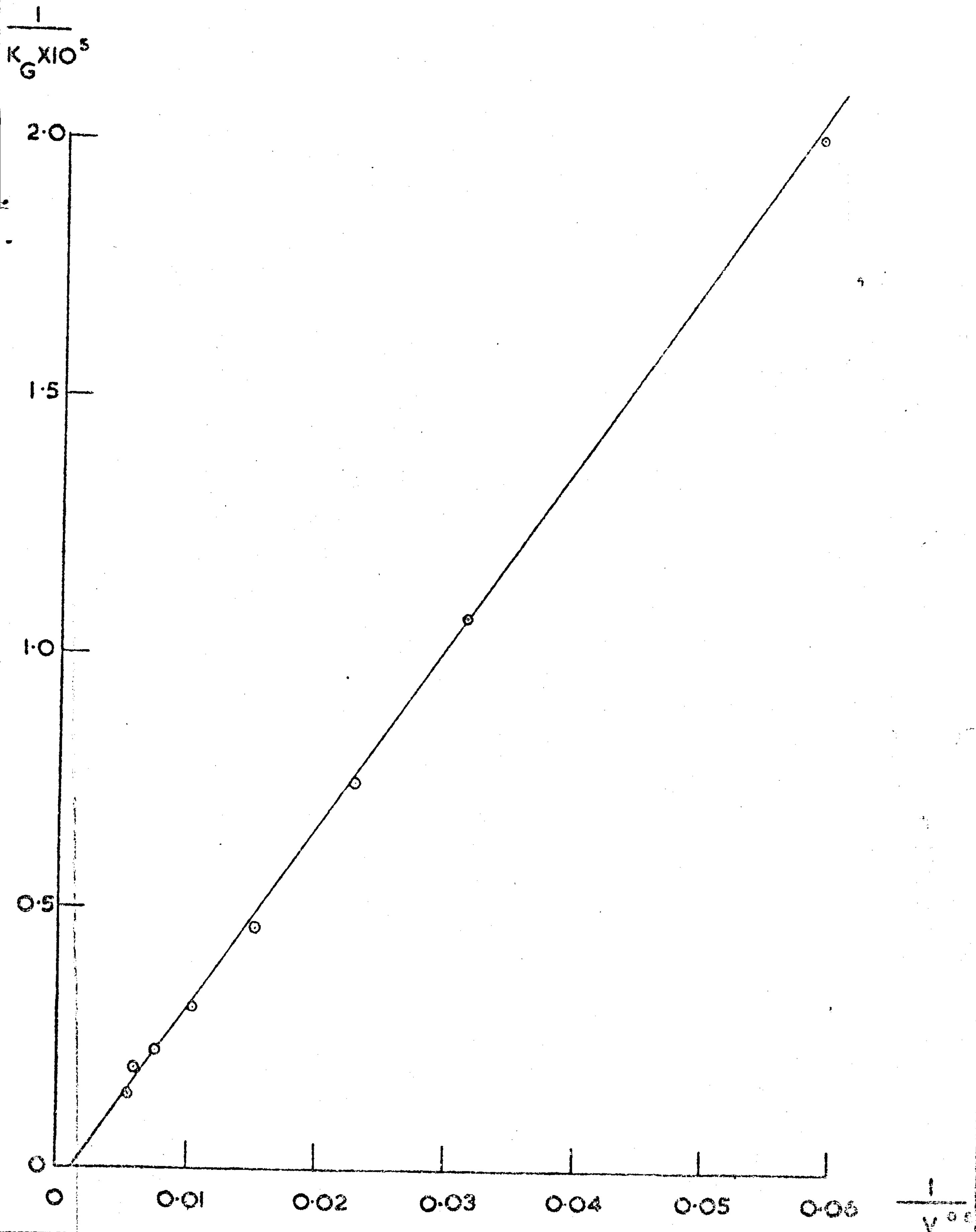
Steam heated evaporators, either of the vertical or horizontal tube type, have been adopted in Europe and U.S.A. the bodies being made of cast regulus with graphite or tellurium lead tubes. Scale formation is a bugbear in these evaporators largely controlled by conditions in the reaction system.

Ancillary equipment, such as spray traps and condensers may be rubber lined, a hard rubber being generally favoured by suppliers, but not of necessity by the user. Attention should be paid to the condenser system, particularly if saline water is used.

Effluent. All gases from the process are trapped. In fact very little is evolved as gas unless deliberate defluorination is attempted. Our gases are absorbed in water washed acid resisting brick towers cemented with quartz filled silicate cement. The liquor is discharged into an effluent flume made of concrete lined with acid resisting brick. A rubber latex cement is used.

Perhaps we may end on a note of caution; the only reliable method of deciding on a material of construction is to try it out.

FIG. 8.



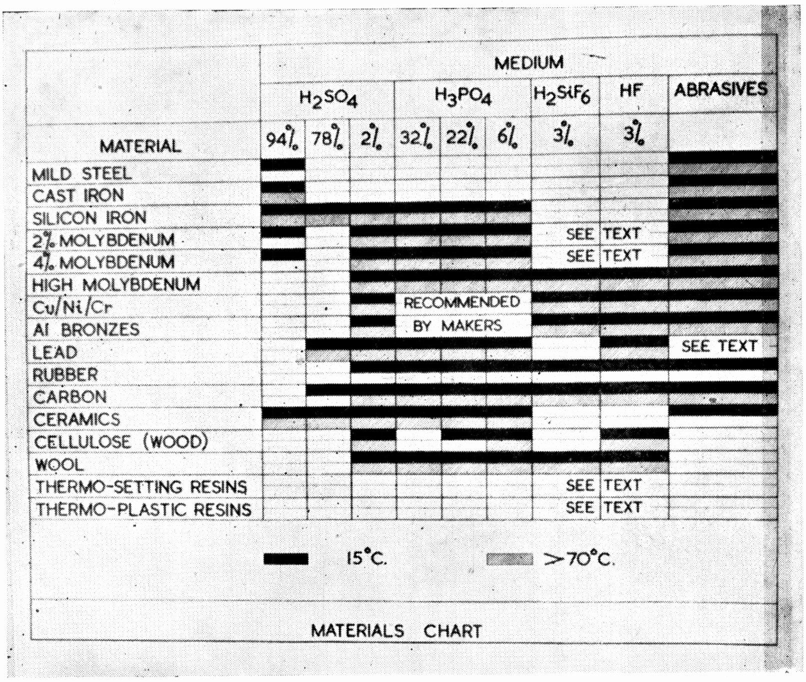


Fig. 1. Resistance of materials to various types of attack.

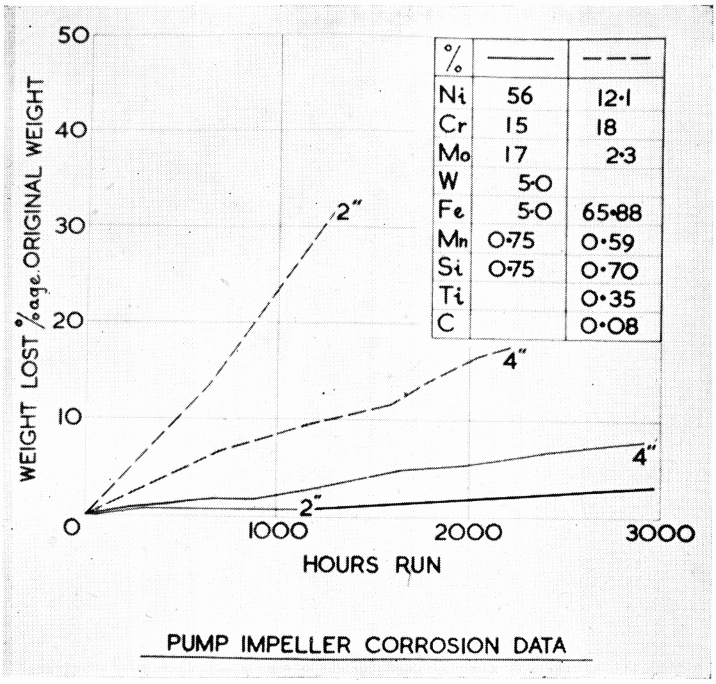


Fig. 2.

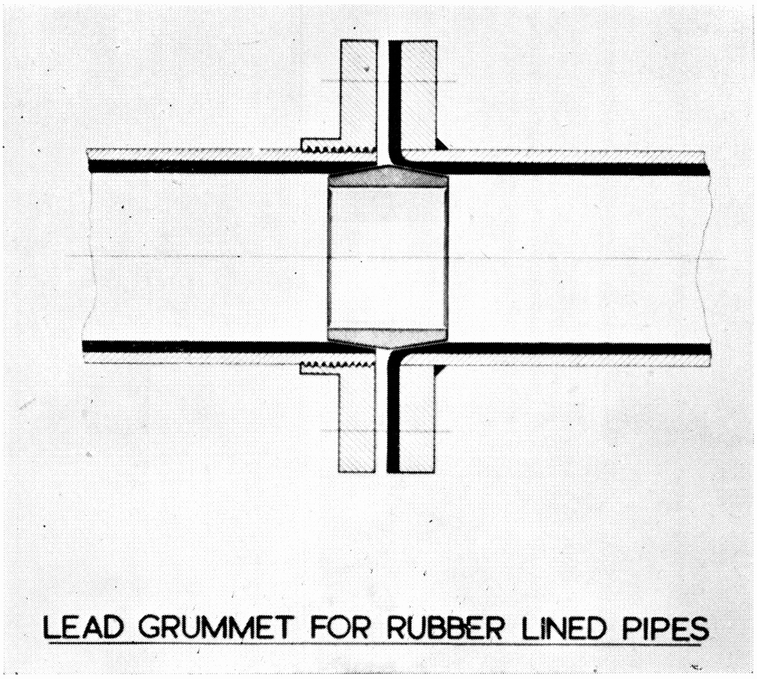


Fig. 3.