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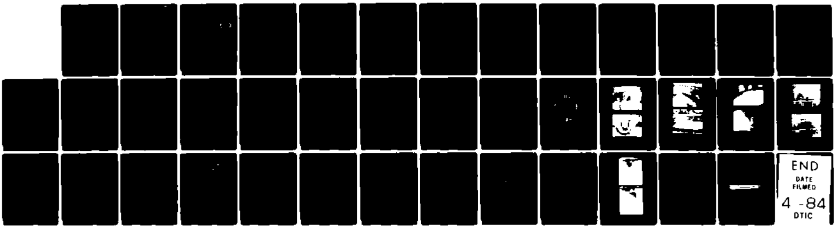

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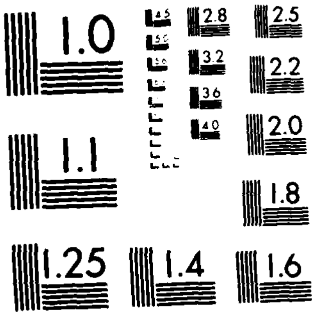
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REPORT

MRL-R-885

CONCENTRATION OF SULPHURIC ACID: PREMATURE FAILURE OF BAMAG POTS

Jeffrey J. Batten & Peter J. Knuckey

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ABSTRACT

In the Bamag process, dilute sulphuric acid (of about 70% strength) is reconcentrated to about 95% by boiling in a cast iron still pot. The acid for reconcentration flows down a packed column (dephlegmator), where its concentration during descent increases progressively, before the partially concentrated acid enters the pot via the base of the dephlegmator. In the pot it is further concentrated by boiling, and the concentrated acid overflows through a run-off pipe into an acid cooler and thence to storage at a rate determined by the input flow. Each pot contains about 10 tons of acid which is boiled and stirred.

The operating life of a Bamag pot should exceed two years, but in recent times at Australian Explosives Factory 'A' several of its operating pots have had a life of less than 5% of this figure. This extremely short life is due to localized corrosion in the vicinity of the outlet at the liquid surface level. This paper examines the main factors that could contribute to this particular corrosion and to such a short life. Observed corrosion problems during operation of similar pots at other plants are also discussed.

It is concluded that the short life of some pots at Factory 'A' is mainly due to weak acid reaching the cast iron walls of the pot, where it quickly causes the localized corrosion that leads to rapid failure. Simple procedures to prevent this are suggested. An attempt is made to deal in some detail with the operation of the plant and an indication is given of the conditions under which it can operate successfully.

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CONTENTS

CONCENTRATION OF SULPHURIC ACID :

PREMATURE FAILURE OF BAMAG POTS

1. INTRODUCTION

Large quantities of concentrated sulphuric acid (approximately 95% acid) are required in the manufacture of explosives such as TNT, nitroglycerine, nitrocellulose, RDX and tetryl. The acid, however, does not become part of the manufactured product but re-appears as a by-product which usually has been diluted with water to about 70% acid. Therefore once concentrated back to 95% acid it becomes suitable for re-use. In the Bamag system, which is a continuous process, diluted sulphuric acid is concentrated in a direct-fired pot concentrator made of cast iron equipped with an agitator. Although the operation is simple in principle, the high boiling point and corrosive nature of the acid, and the possible evolution of acid fumes and mists during concentration, present many difficulties.

The expected life of the Bamag pots is usually quoted [11,19,21,26,27] as being in the range from six months to over three years. Working lives as short as six weeks and up to seven years appear to be the exceptional extremes [14,18]. The failures reported in the literature have been generally attributed to three main causes:

(i) general thinning of the walls of the pot at the liquid/vapour interface, attributed to weak acid (i.e. of strength < 95%) coming into contact with the walls,

(ii) thinning of the bottom of the pot, which is generally attributed to erosion, and

(iii) cracking due to thermal stress.

General overall corrosion, resulting in thinning of the walls, usually does not lead to failure.

Over the past ten years or so, Australian Explosives Factory 'A' has been experiencing serious production problems in their sulphuric acid concentration plant. A major one has been due to the rapid failure of quite a few of their Bamag pots where, instead of the above expected life of at least six months, the operating life has been of the order of one month with, however, one extraordinary failure after 16 days. This has led to serious financial losses due to the high cost of pots and serious loss of production.

The purpose of this paper is to identify the cause of the above rapid failure of the Bamag pots and to suggest remedial measures to overcome the problem.

2. GENERAL DESCRIPTION OF THE BAMAG PROCESS AS PRACTISED AT AUSTRALIAN EXPLOSIVES FACTORY 'A'

In the concentration of sulphuric acid to about 95% strength, acid of about 70% enters the top of a dephlegmator and in descending the packed column it meets an escaping high temperature atmosphere of steam and sulphuric acid vapour produced by the initial mixing in the still. The temperature and concentration of the descending acid thus increases progressively as it passes down the dephlegmator to render the process more efficient. The partially concentrated acid then enters the pot at the base of the dephlegmator and drops onto a relatively large volume of agitated boiling concentrated acid. Final concentration of the weaker acid is now achieved by rapid evaporation of its water and by mixing it with the stronger acid.

The cast iron pot shown in Figure 1 is approximately 8 feet (2.4 m) diameter by 6 feet (1.8 m) deep and contains about 10 tons of acid. The cover of the pot is also an iron casting including openings for dephlegmator, stirrer, and manhole. Both pot and cover are made of medium/low strength unalloyed flake graphite cast iron. The thickness of the pot at the acid surface line is about two inches (51 mm). The acid in the pot is kept boiling at about 315°C by heating the pot externally with oil fired burners. The stirrer, made from silicon iron, operates at about 30 to 40 r.p.m. in a clockwise direction (looking down on the pot). It will be noted that the concentrated acid flows away through a peripheral outlet aperture located at the acid surface line. If we refer to this acid outlet as being located at 12 o'clock, then these pots have usually been operated in Factory 'A' with the acid inlet also at 12 o'clock (as indicated in Figure 1). In recent times each pot has usually operated at an output rate of between 25 and 30 tons per day.

3. NATURE OF THE MAJOR CORROSION PROBLEM AT AUSTRALIAN EXPLOSIVES FACTORY 'A'

The nature of the premature failures of Bamag pots at Plant 'A' in each case was virtually identical. Very localized perforation of the pot walls had occurred in close proximity to the concentrated acid outlet, but usually higher than it. Severe "line" attack extending for as far as one meter on either side of the outlet and at about the same level as the outlet is generally also observed. Figure 2a is an external view of a prematurely failed Bamag pot (the above-mentioned 16 day failure), while Figure 2b graphically shows three perforations near but higher than the outlet in detail. Figures 2c and d show very clearly the localized nature of the attack. These latter two photographs also show a ring that extends completely around the pot for supporting acid-proof tiles [8], but the use of tiles went out of favour many years ago. Also in Figure 2d can be seen cast-on brackets for attachment of a cowl [8], as discussed later. This figure does illustrate very clearly that there appears to have been no significant thinning of the metal by the boiling concentrated acid on these appendages for the cowl. Figure 2c also shows that in this particular case the concentrated acid outlet protruded 50 to 80 mm within the pot - the extent of this protrusion appears to be random from pot to pot.

Figure 3a is an internal view of the outlet of another prematurely failed pot and shows clearly two perforations above the level of the acid outlet, together with a line attack at about the same level as the outlet. This line attack, which extends about one quarter of the way around the pot from the outlet, is shown clearly in Figure 3b. (It will be noted that there are no obstructions to the flow of the acid in the interior of this pot, i.e. it has a smooth interior - this point is discussed later.)

In this regard Figures 4a and b are interesting for they show the corrosion pattern inside a partially-used pot where the concentrated acid outlet protrudes about 100 mm inside the pot. The influence of this obstruction to the flow is clearly visible through the pattern created by the corrosive attack.

The important point to notice is that in each of the above corrosion patterns associated with prematurely failed pots, it is a very localized attack of the cast iron at the liquid/vapour interface, in the vicinity of the concentrated acid outlet pipe.

4. THE NORMAL BEHAVIOUR OF CAST IRON IN BOILING CONCENTRATED SULPHURIC ACID

4.1 Laboratory Measurements

The rate of attack of boiling strong sulphuric acid on cast iron, plotted against acid concentration, is shown in Figure 5. It is clear from this figure that slight changes in acid concentration have a very pronounced effect on corrosion rate [21] and a change in acid concentration from 98 to 92% results in a rate change from insignificant to dramatic. Cast iron possesses no useful resistance to dilute sulphuric acid [14,19,20]. A more complex relation between corrosion and temperature in Figure 6 indicates, however, that for 96% sulphuric acid in the vicinity of its boiling point, the rate of corrosion of cast iron is not very sensitive to small changes in temperature [18].

It should be emphasized, however, that the graphs in Figures 5 and 6 are derived from laboratory measurements. Those rates normally found in practice on immersed surfaces of well-seasoned pots are consistently lower. The graphs are reproduced solely to indicate the trend in corrosion rate. It is clear, certainly, that cast iron will withstand the action of concentrated sulphuric acid satisfactorily only within certain limits.

The passivation of cast iron to the attack of concentrated sulphuric acid is attributed to the formation of an iron sulphate film over the entire metal surface [9,10,14,16,18,20] which is insoluble in strong sulphuric acid. The resultant low rate of attack is shown for concentrations of sulphuric acid greater than 97% at temperatures of about 300°C which have corrosion rates of about 0.12 mm/y.

4.2 Plant Experience

As the above-mentioned protective film does not form instantaneously, the attack on a new pot is fairly rapid. This soon decreases, however, and the common experience is that after a period of 12 to 36 hours from commissioning the corrosion subsides [9,10,14,25] and the concentrated acid becomes progressively less "milky". This type of passivation means that it is generally considered desirable to give new pots with stirrers a preliminary treatment with concentrated acid at rest so that a better protective layer may be formed. Any influence which militates against the formation or retention of the insoluble sulphate film may lead to excessive local corrosion rates. High liquid velocity, or abrasion of the metal surface, fall into this category. However the film can reform at breaks in the surface caused by erosion or cracking.

The normal reasonable life, 2 to 3 years, of a seasoned cast iron pot in acid of about 95% strength, together with the desirable mechanical properties and cheapness of cast iron, give the economic justification for the choice of cast iron for this service. But use of cast iron does have the drawback which normal plant experience has shown: more dilute sulphuric acids at their boiling-points are extremely corrosive to cast iron pots, and it is generally undesirable to use these pots in contact with any hot sulphuric acid solution if the water content is more than about 10% [19,20].

5. CORROSION DIFFICULTIES EXPERIENCED IN OTHER SIMILAR SULPHURIC ACID CONCENTRATION PLANTS

This section outlines briefly corrosion experiences of other similar plants considered relevant to the observed premature failures of the Bamag pots. It is very clear from the literature [1,2,8-11,14,15,18,21,22,26] that the experience of similar plants operating on a continuous basis shows the operation of these cast iron vessels to have a number of problem areas that must be attended to.

5.1 *Early Concentrators and Their Corrosion Difficulties for the Period 1898-1910*

The nature of these difficulties may be gauged from patents for this period [1,2]. Many of these aimed at preventing dilute acid from contacting the pot walls by providing shields of stoneware or high silicon iron at the liquid surface level, or by allowing the dilute acid to enter the pot under the level of the concentrated acid. In some systems provision was made to ensure that only the strongest acid from the bottom left the pot either by a tube passing upwards through the acid or by means of a siphon.

5.2 *Corrosion Difficulties Experienced in the Dreyfus Process (1916)*

In a Dreyfus Process plant (see Figure 7a), sulphuric acid of 93% was concentrated to 96.5% in cast iron pots 3 ft 4 1/2 in. deep by about 3 ft 6 1/2 in. mean diameter [1,2]. It will be observed that the 93% acid drops from the centre of the lid on to the concentrating acid, and that the concentrated acid is taken from the bottom. A special cast iron shield was provided at the top of the pot to arrest corrosion at the acid line.

One plant worked continuously for about twelve months when it was observed that corrosion of the pots had occurred on the acid line behind the shield. This difficulty was overcome effectively by increasing the wall thickness in the vicinity of the acid level from 2 1/2 inches to 4 inches as shown in Figure 7b. This plant (consisting of 4 pots) was capable of concentrating 18 tons per day of sulphuric acid from 93% to 96.5%.

5.3 *Modifications to the Concentration Plants : The Bamag Patents (1940/41)*

5.3.1 *First Bamag Patent*

This patent [6] describes "an apparatus for concentrating sulphuric acid in cast iron pots, where there may be a tendency to deposit suspended or produced solids". The invention describes a rotary stirring device or paddle (see Figure 8) to maintain the sediment in a freely suspended or distributed state. In particular, there is a means of raising and lowering the stirring device from and to the bottom of the vessel.

5.3.2 *Second Bamag Patent*

This patent [7] describes a process in which the acid is partially concentrated in a dephlegmator, and then passes to the still where it is finally concentrated without mechanical agitation. The concentrated acid passes out of the still through a siphon dip pipe which extends from the bottom of the still through the wall at the liquid level (see Figure 9).

5.3.3 Third Bamag Patent

The object of the invention [8] is to minimise the effects of inefficient mixing in an apparatus where the weak acid is introduced through an aperture in the cover on to the surface of the concentrating acid and the concentrated acid flows away through a peripheral outlet aperture. To this end a cowl (preferably removable) is placed over the outlet aperture and extending adjacent to the wall of the still to well under the acid liquid level. This arrangement provides a substantially closed passage for concentrated liquid from the bottom or lower part of the still to the outlet aperture. Such an arrangement is shown in Figure 10.

In such a still the action of a rotary stirrer with angled blades produces a convection current falling in the centre and rising about the periphery. The purpose of this current is to ensure that the incoming weak acid is incorporated rapidly in the contents of the still and that the overflow will consist only of the concentrated acid. The patent addresses itself, however, to the disadvantageous possibility of the incoming weak acid splashing directly into the vicinity of the outlet aperture and passing over in quantities large enough to reduce the average concentration of the output. Further, this possibility could be compounded by the bubbling action of the boiling acid militating against the effectiveness of the mixing of the convection current by the stirrer.

It will be appreciated that in these sulphuric acid stills the cowl is directly exposed to attack by the incoming weak acid. Although it is possible to protect an integral cowl (e.g. by brickwork) it is preferable to provide a cowl member that is cheaply and conveniently replaceable. To this end the cowl is usually a simple casting; it may be a ferro-silicon casting, or an acid resisting iron casting or even an ordinary grey iron casting. It is pertinent to note that the arrangement for supporting the cowl (see Figure 10) appears to be identical with that shown in Figures 2d and 15.

5.4 Concentration Plants as Reviewed by Parrish (1941)

These reviews [9,10] outline the state of the art at 1941 for the design of plant for the concentration of sulphuric acid. In the first paper [9] a diagrammatic sketch is given of a cast iron pot-dephlegmator concentrator (see Figure 11). The cover over the outlet aperture in this pot is similar to the cowl described in the Bamag Patent [8]. Note that the weak acid inlet to the pot and the concentrated acid outlet are both located at 12 o'clock.

The main review [9] examines in some detail aspects of design of two other contemporary (1941) sulphuric acid concentrating plants and also states that in Britain since 1937 most of the plants have had a rated capacity of about (but less than) 20 tons per unit per day. In the first design discussed, the pot of 7 feet internal diameter has an external swan-neck outlet (see Figure 12), and a rated capacity of 10 to 12 tons of concentrated acid per unit per day. The second design (see Figure 13) has a pot of 7 ft 9 in. internal diameter (i.e. about the same as that at Factory 'A') with submerged outlet and stirring gear. These latter pots had a rated capacity of 12 1/2 to 16 tons of 96-97% H_2SO_4 per unit per day. Note in particular in Figure 13 that the dilute acid inlet is located at 6 o'clock to the submerged concentrated-acid outlet (cf. Bamag patent [7] and Figure 9).

Mention is also made here (see Section 4) of the protective influence of sulphate of iron to the skin of the cast iron pot [14,16,18]. It is also stated in these reviews that with these processes there is always a tendency for corrosion to occur on the liquid/vapour interface. For this reason some chemical engineers prefer to line the pot at this critical point with acid- and heat-resisting tiles, whereas the practice in other cases has been to thicken the castings at this point (see above Section 5.2 and Figure 7b).

Parrish then discussed the nature of the outlets of these cast iron vessels. Thus, for example, he states that an externally-arranged outlet (see Figure 12) necessitates a core, and may conceivably cause difficulties in casting. Also, when renewing a swan-neck (Figure 7a) it is necessary to syphon out the acid, whereas with the submerged internally-arranged outlet (Figure 13) only part of the acid needs to be removed.

5.5 *Problems of The Pauling Process (1979)*

In an extensive review article [25], Bodenbenner et al. refer to the Pauling Process for regenerating spent sulphuric acid. It is clear from the diagrams and references quoted (e.g. [9] and [12]) that it is, in fact, identical with the Bamag Process for converting 70% acid to 95% acid.

The paper states that the life of the boiler (12 tons per day, H_2SO_4) at Hoechst in the years 1937 to 1943 was (on the average) two years without detailing the causes of failure. However, with the introduction of a new series of burners, a boiler life of about four years at 15 tons per day sulphuric acid was achieved. This latter design appears to be a boiler with an inside diameter of about 2.4 m and a depth of about 2.1 m and with an output of 22 tons per day. The wall thickness of the hemi-spherical bottom is about 65 mm and that of the sides about 50 mm. On measurement with radioactive lanthanum, this boiler at 22 tons per day and stirrer speed of 32 r.p.m. proved to be "ideally mixed". Under these conditions the average corrosion rate of the material of this boiler, pearlitic grey cast iron with lamellar graphite structure, was 8 to 10 mm/year. It is also stated that in addition to the uniform corrosion of the boiler surface, the formation of deep grooves is occasionally observed, especially at the liquid/vapour interface. The further claim is made that the cause of this phenomenon is unknown.

This paper states that nowadays (1979) stirrers are built in to boilers with an output above 8 tons per day of sulphuric acid, where stirring the contents is intended to prevent a deposit of iron sulphate sludge and to improve heat transmission. They operate at a speed of about 30 r.p.m.

6. DISCUSSION

We have seen that localized corrosion of the cast iron pots is a major problem in the operation of these sulphuric acid concentration plants at Factory 'A'. It is of interest, therefore, to examine factors in the operation of this and other plants which are assumed to alter the corrosion rate of cast iron in boiling sulphuric acid, paying particular attention to possible factors which could produce localized perforation of the cast iron pots and thereby reduce their life.

Clearly chemical engineering processes which appear at first to be sound may, in actual operation, give rise to difficulties from what may appear to be only minor causes. If these difficulties persist production suffers, and at that stage there is a clear justification to examine procedures and/or equipment being used.

6.1 Operational Factors that Could Cause Failure

Operational factors which may be expected to influence the position and rate of corrosion of cast iron, and so contribute to the wide scatter in pot life, are:

(a) variations in acid concentration (e.g. Figure 5);

(b) variations in acid temperature (e.g. Figure 6);

(c) changes in the nature and concentration of impurities in the acid;

(d) variations in the composition and microstructure of the cast iron;

(e) faults in the casting resulting in internal cavities;

(f) an influence, for example high liquid velocities or abrasion of the metal surfaces, operating against the formation or retention of the insoluble protective sulphate film, thus leading to excessive corrosion rates at high acid concentrations.

6.2 Factors Observed in Factory 'A' Failures

The following observations concerning the observed premature failure by corrosion of the Bamag pots at Factory 'A' are considered pertinent to the elucidation of the actual mode of attack.

> Firstly, a rate of attack on cast iron of about 50 mm per month (i.e. the average life at Factory 'A' for many of their pots) corresponds to about 600 mm/y, which is about a ten-fold increase on that expected for boiling 95% sulphuric acid (see Figure 5).

Secondly, the attack is very localized. Thus, for example, in Figure 2 it is very clear that although there has been perforation of the 50 mm thick wall of the pot, near-by protrusions attached to the wall of the pot appear to be unattacked. This emphasizes the much higher corrosivity of the surface layers compared with the bulk acid. The corrosivity gradient is extremely high.

Thirdly, the corrosion pattern from pot to pot is usually very similar, namely localized attack resulting in perforation close to the concentrated acid outlet and usually at a level higher than it, concomitant with severe attack at the liquid surface level for about a meter on either side of the outlet.

Fourthly, the above corrosion pattern is independent of the manufacturer of the pot.

Lastly, the corrosion pattern is not significantly affected by whether or not there are internal appendages within the pot.

6.3 Analysis of Failure Causes

Taking into consideration all the above observations, and in particular the localized nature of the attack and the similarity of the effect on different pots, it is concluded that factors (c), (d), (e) and (f) listed above in Section 6.1 will not significantly contribute to the observed abnormal short pot life. For example, no evidence of (c) being a factor has been found in the literature. Similarly, it has been shown that microstructure or chemical composition of cast iron (i.e. (d)) have little effect on corrosion rate [21,25]. Further, these pots are usually tested for internal cavities (i.e. factor (e)), either by the hammer test [9] or by radiography, before being used. Finally, (f) is too wide ranging to be an explanation.

Factor (b) may also be readily eliminated. As shown by Figure 6, a slight cooling from the normal operating temperature possible in the region of the outlet (i.e. where the perforation occurs) could not yield the observed excessive corrosion rates.

Factor (a) cannot be readily eliminated however. At the boiling point of 95% acid, slight changes in acid concentration have a very pronounced effect on corrosion rate as is shown clearly in Figure 5. For instance the observed corrosion rate of about 600 mm/y may occur if 92% acid reaches the walls of the cast iron vessel.

It is our conclusion, therefore, that the most probable cause of the extremely high corrosion rate observed has been acid of strength less than 95% (e.g. 92%) coming in contact with the pot wall, the localized nature of the attack being dictated by the flow conditions existing during normal operation.

6.4 Discussion of Mixing as it Occurs in Bamag Pot 'A' in Particular

We consider that, to mitigate the observed localized corrosion at the liquid surface level, it is necessary to improve the rate of concentration of the weak acid after it falls from the dephlegmator on to the surface of the much larger volume of boiling 95% acid in the pot. This rate of concentration would appear to be governed by two main factors. These are, *firstly*, the rate of heat transfer to this acid, and *secondly*, the efficiency of mixing.

It is quite well appreciated that the subject of mixing is one of the most difficult of the unit operations of chemical engineering to submit to scientific analysis [28-31]. It will be observed from Figure 1 that the present mixer at Factory 'A' is of the impeller type with the blades pitched and with the impeller rotating in the centre of virtually unbaffled vessels (i.e. vessels with no, or very few internal appendages (cf. Figures 1, 2 and 3)). We have observed the flow pattern of the acid within these vessels at Factory 'A', admittedly (and of necessity) with the concentrated acid cold, and have found that a deep vortex was formed around the shaft at impeller rotational speeds of 30 to 40 r.p.m (see Section 2 above). This pattern indicates that the liquid is being pushed both radially and tangentially. Thus it is clear that a centrifugal force is acting on the fluid raising the fluid level at the wall and lowering the level at the shaft. The above pattern is in agreement with that stated in the Bamag patent [8].

Let us consider in more detail the flow pattern in the liquid created by such an impeller. In general, of course, the liquid circulates *through the vessel*, returning eventually to the impeller. Circulation by itself, however, is not the only important factor in mixing, for it is possible to have streams or currents travel side by side for some distance with little or no intermingling. Turbulence in the moving stream is the second important mixing factor. Turbulence provides the means of entraining material from the bulk and incorporating it in the flowing stream. The greater the turbulence the more rapidly the dilute acid is mixed and therefore concentrated.

The velocity of the fluid at any point in these pots with their centrally located impeller, and with the concentrated acid outflow located on the liquid/vapour interface, has three components (as illustrated in Figure 14) and the over-all flow pattern depends on the variations in these three velocity components from point to point. The first velocity component is *radial*, and acts in a direction perpendicular to the shaft of the impeller. It might be expected that this component, at least in the surface layers of the acid, would be influenced by the presence of the above type of acid-outlet and may, therefore, not be radially symmetrical. Also the radial component outwards and on the surface maintains hydrostatic pressure at the vessel wall. Thus it is the authors contention that there is a surface radial component of the flow that is considered to be the major cause of the corrosion problem. The second component is *longitudinal* and acts in a direction parallel with the shaft. The third component is *tangential*, or rotational, and acts in a direction tangent to a circular path around the shaft.

It is clear from Figure 14 that the radial and tangential components are in a horizontal plane, and the longitudinal component is vertical. The *radial and longitudinal components are useful*, and provide the flow necessary for the mixing action. The *tangential component is generally disadvantageous*, for the tangential flow follows a circular path around the shaft, creates a vortex at the surface of the liquid and tends to perpetuate, by a laminar-flow circulation, stratification at the various levels without accomplishing longitudinal flow between levels.

Swirling may be reduced by installing baffles (such as vertical strips installed perpendicular to the wall of the pot) which impede tangential flow without interfering with radial or longitudinal flow. However erosion of baffles could then be a problem.

7. ANALYSIS OF OPERATIONAL DATA AND CONCLUSIONS

7.1 Possible Cause of Corrosion Problem

From the nature of the observed corrosion pattern within these pots, it is suggested that the major part of the present problem is due to the rate of concentration of the dilute acid (brought about by heat transfer from the 95% acid and by mixing) being too slow to cope with the radial velocity component of the dilute acid in the general direction of the inner wall of the pot and the outlet. The result of the imbalance between the rate of concentration and the efficiency of mixing is that at least some of the dilute acid has not been concentrated to 95% and is still on the surface of the concentrated acid when it comes into contact with the wall of the pot in the vicinity of the outlet and at the liquid surface level. Contributing to this is the surface radial velocity component towards the outlet that effectively transfers weak acid to an area where its corrosion properties come into play.

The following changes in the operating procedure are suggested as a means of overcoming the problem, where their aim is to allow adequate time for the weak acid to be concentrated before it has a chance of contacting the walls of the pot at the liquid surface level in the vicinity of the outlet. To this end, in order to minimise the above chance, the over-all rate of movement of dilute acid in this general direction must be reduced while it is being concentrated.

7.2 Possible Remedy of the Problem

It is suggested that the above-defined adequate time would be achieved if:-

(a) The effective acid outlet was located in the body of the acid, as illustrated in Figure 13 - this would remove the influence of the outlet on the surface radial velocity component (as discussed earlier);

(b) the path between where the dilute acid landed on the surface of the 95% acid and the acid outlet were at a maximum, for example if the inlet was at 3 o'clock to the outlet (see Section 2); and

(c) the rate of admission of weak acid was reduced - by heat transfer principles, a thin layer of weak acid on the surface of the 95% acid would lose water and concentrate more quickly than a thicker layer by heat transfer alone.

On the other hand, it would not be expected that adequate time be achieved by increasing the impeller rotational speed as this would increase the surface radial velocity component.

7.3 *Comparison of Remedy with Literature Search of Operational Procedures*

In the light of the above suggestions we have examined the general practice for the successful operation of these plants, as deduced from the published literature, to ascertain whether or not there is a consensus opinion for their successful operation, and to compare this consensus with our recommended alterations to the operating procedure. The result of this examination is presented in Table 1.

It is clear from this table that the main differences between Factory 'A' and the other plants arise in points 4, 5 and 6 (see table). It should be noted that the suggestions (a), (b) and (c) listed above bring Factory 'A' into line with the generally found successful operating procedures of other plants.

7.4 *Engineering Aspects*

From the point of view of casting these pots and their subsequent operation, there are certain advantages for having a simple outflow at the liquid surface level as at Factories 'A' and 'B' (see table). However, it will be noted in the table that not one of the designs of plants reported in the literature, whether agitated or not, has an outlet of this type - they are all external or internally-submerged outlets.

In this connection, the original Bamag specification [8] called for a cowl to block-off the outlet aperture from surface layers of acid (see earlier). The cowl was shaped to accommodate any internal protective ring of tiling at the level of the outlet aperture (as shown in Figure 10). Hence the cowl shown in Figure 15 would not be very effective because there is a 55 mm gap between the upper section of the cowl and the vessel wall. Such a cowl could be made satisfactory, however, by appropriate welding of metal to it to fill this gap or by making the castings of the appropriate shape.

7.5 *Summary*

The correlation of all the existing published data (Table 1) concerning the difficulties encountered using cast iron pot concentrators allows it to be concluded that the prime cause of the observed localized corrosion in Factory 'A' was due to acid of strength less than 95% coming into contact with the pot at the liquid/vapour interface in the vicinity of the concentrated acid outlet.

It is evident that more generalised corrosion can also occur at the liquid/vapour interface. Two remedies for this have been suggested, namely lining the pot at this critical point with acid resisting tiles, or thicken the casting at this point. Of these two procedures, the latter is the preferred.

It is further concluded that the handling of hot sulphuric acid is always attended with some risk and so in any plant modification it is important that extreme care should be given to all details of the plant and its operation. To this end, there can be little doubt that a skilled chemical engineer is required for such an operation.

8. RECOMMENDATIONS

It has been concluded that this corrosion problem could be minimised by modifying the operation of the plant, and to this end the following modifications are recommended:-

(a) The effective concentrated acid outlet should be moved to the body of the acid.

(b) The acid throughput should be reduced to about 20 tons per unit per day.

(c) The dilute acid inlet should be located to give the longest path (and hence the longest time) between where the dilute acid lands on the surface of the concentrating acid and the concentrated acid outlet.

(d) Consideration should also be given to introducing the dilute acid from the dephlegmator into the pot below the bulk acid level (cf. Section 5.1). This should increase the degree of contact between the dilute and bulk acids, thus increasing the concentration rate.

(e) Consideration should be given to increasing the wall thickness of the casting at the liquid surface level from its present 50 mm to in excess of 100 mm.

(f) The impeller rotational speed should be maintained at that presently used. However consideration should be given to optimizing stirrer design and operating conditions to improve mixing rate, particularly the vertical component (cf. Section 5.5).

The efficient and economical concentration of weak sulphuric acid demands a plant combining a rational compromise of the above factors.

9. ACKNOWLEDGEMENTS

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TABLE 1

COMPARISON OF THE OPERATING CONDITIONS AT PLANT 'A' WITH THOSE AT OTHER ACID CONCENTRATING PLANTS

Australian Explosives Factory 'A'	Australian Explosives Factory 'B'	Consensus from Literature	Ref.
1. Normal Working Life of Pot			
For a large number recently, about one month.	In excess of two years.	Six months to in excess of three years.	11,14,18, 19,21,25, 26,27
2. Mode of Failure			
Localized attack resulting in perforation in the vicinity of the outlet.	Failures have been reported due to corrosion at the liquid surface level, also through thinning of the bottom due to stirring of debris, and also by cracking due to thermal stress accentuated by corrosion.		11,12,21, 26,27
3. Nature of Pot Wall at Liquid Surface Level			
Cast iron walls, two inches thick with no special provision to protect the walls.	As at Factory 'A'	Lining of the pot at the liquid surface level with acid resistant tiles, or increased wall thickness of four inches.	1,2,9,10, 12,14,18, 21,27
4. Nature of Acid Outlet			
Direct overflow at liquid/vapour interface.	As at Factory 'A'	Submerged outlet (see Figures 7,9,12,13).	1,2,7,8,9, 10,11,13, 14,27
5. Relative Location of Weak Acid Inlet and Concentrated Acid Outlet			
Both located at 12 o'clock - as shown in Figure 1.	Acid inlet located at 6 o'clock with respect to acid outlet.	As at Factory 'B' or inlet as far removed from outlet as possible (see Figures 7,9,12,13).	1,2,7,8,9, 10,27
6. Acid Throughput			
25 to 30 tons per unit per day.	20 tons per unit per day.	$12\frac{1}{2}$ to 22 tons per unit per day.	1,2,9,10, 11,25,27
7. Impeller Rotational Speed			
Usually 33 r.p.m. sometimes up to 46 r.p.m.	About 30 to 32 r.p.m.	About 30 to 40 r.p.m.	12,21,25, 27

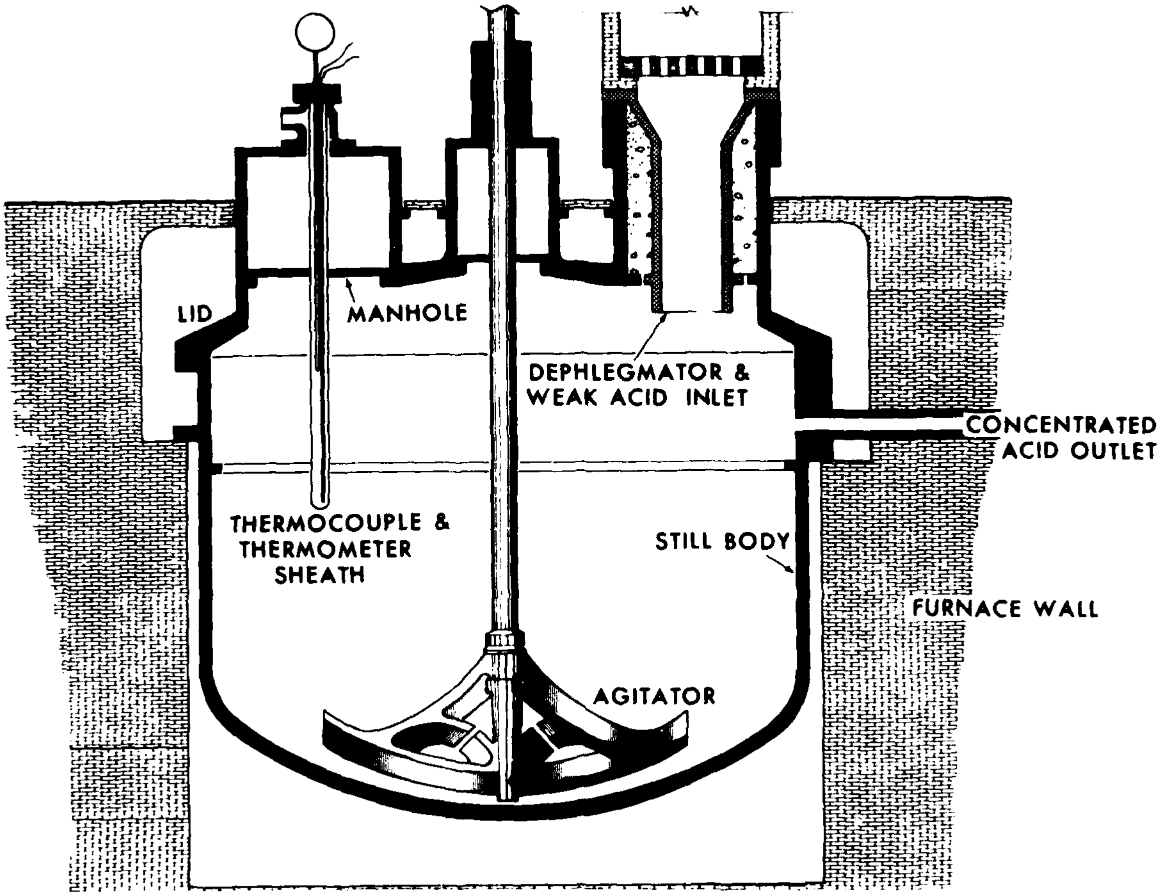


FIG. 1 Simplified version of an engineering drawing of the sulphuric acid concentrator used at Australian Explosives Factory 'A', showing the cast iron pot, the impeller, dephlegmator, and the concentrated acid outlet.

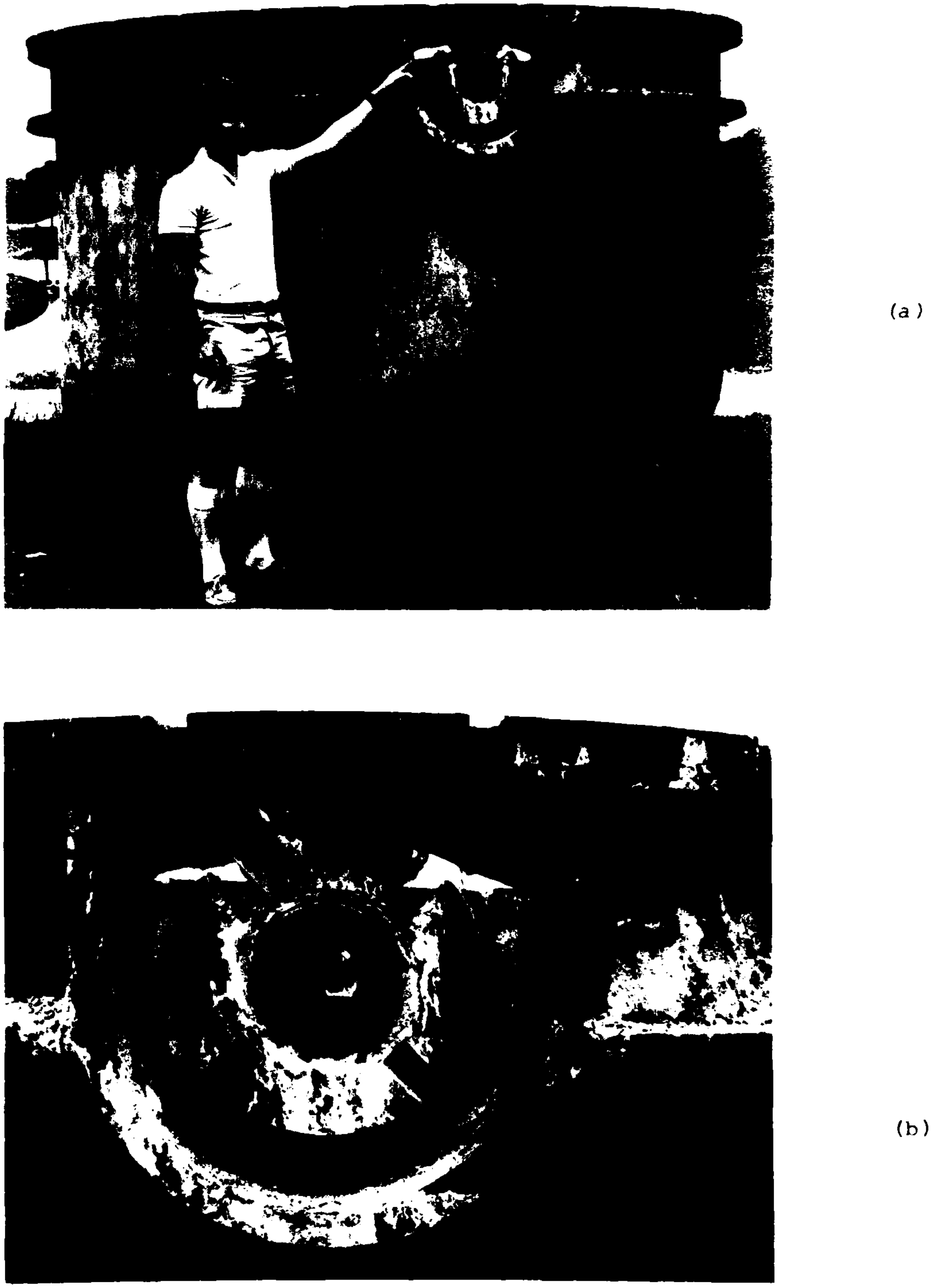


FIG. 2 A prematurely failed Bamag pot at Factory 'A'.

(a) Exterior view.

(b) Close-up of three perforations above the level of the outlet.

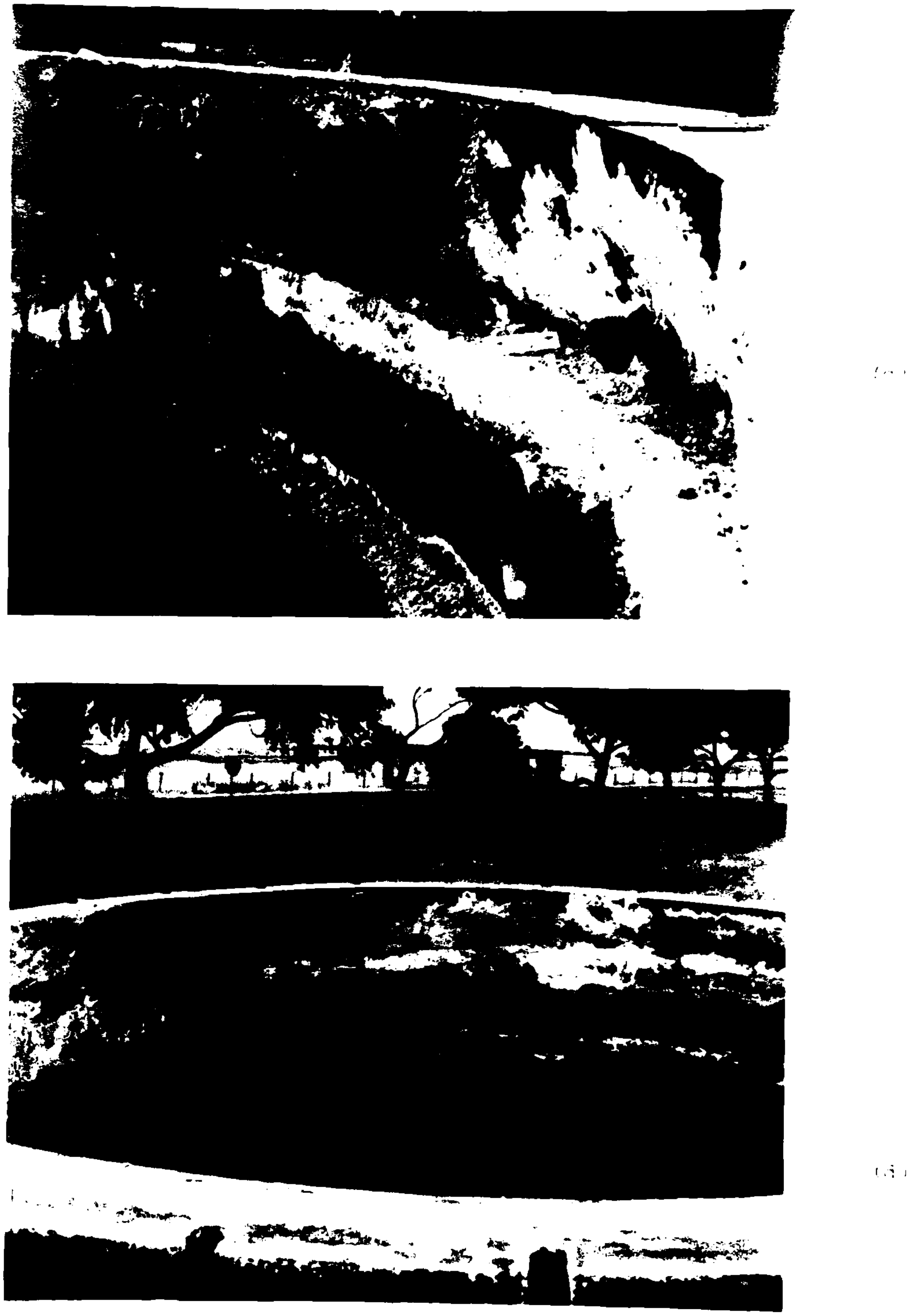


FIG. 2 A prematurely failed Bamag pot at Factory 'A'.

(c) Note the localized nature of the attack and protruding outlet pipe.

(d) General view of the inside of this pot showing a ring, two brackets and two abutment ridges (see text for explanation).

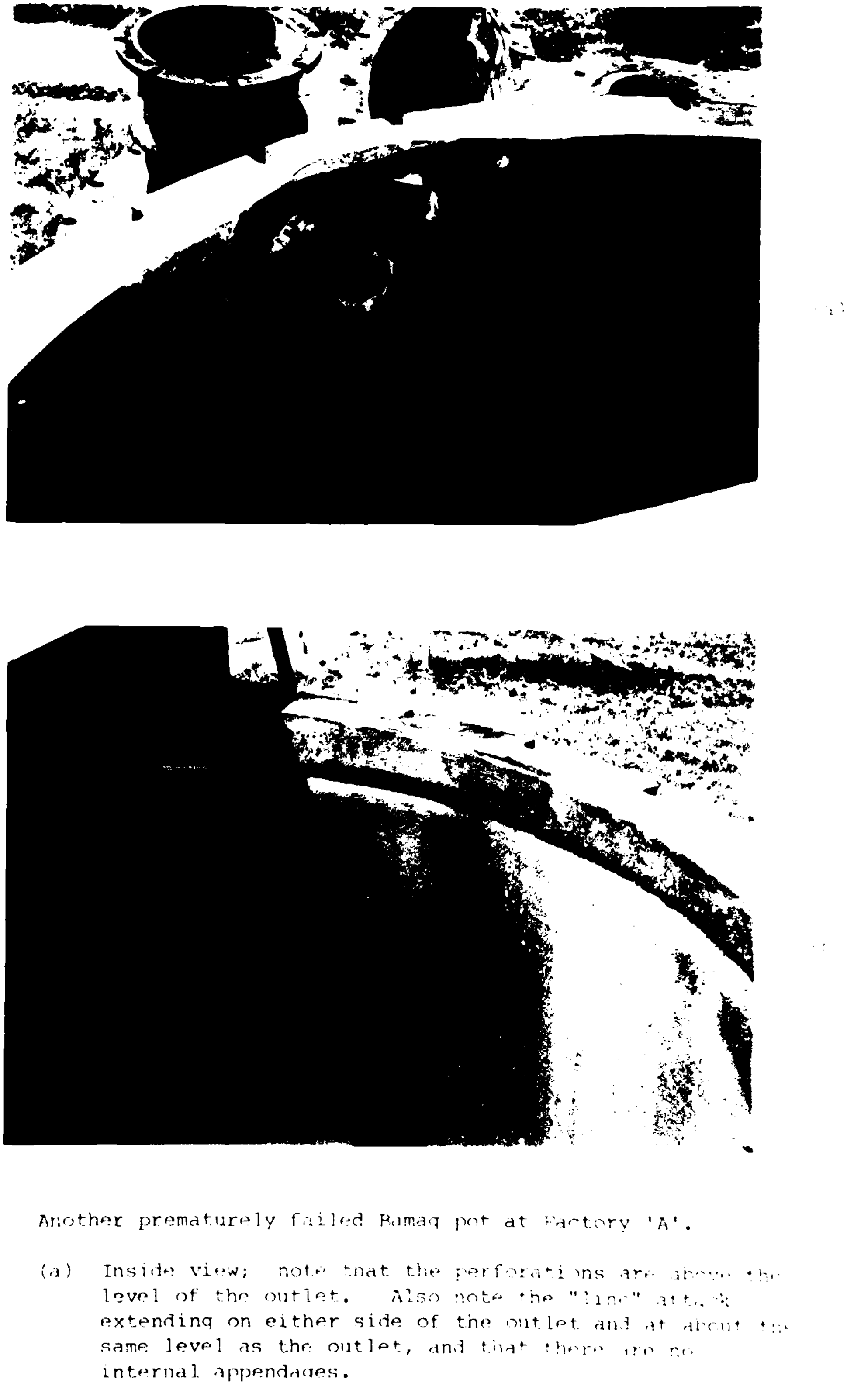


FIG. 5 Another prematurely failed Bamag pot at Factory 'A'.

(a) Inside view; note that the perforations are above the level of the outlet. Also note the "line" attack extending on either side of the outlet and at about the same level as the outlet, and that there are no internal appendages.

(b) The above line attack about 1/4 of the way around the pot.

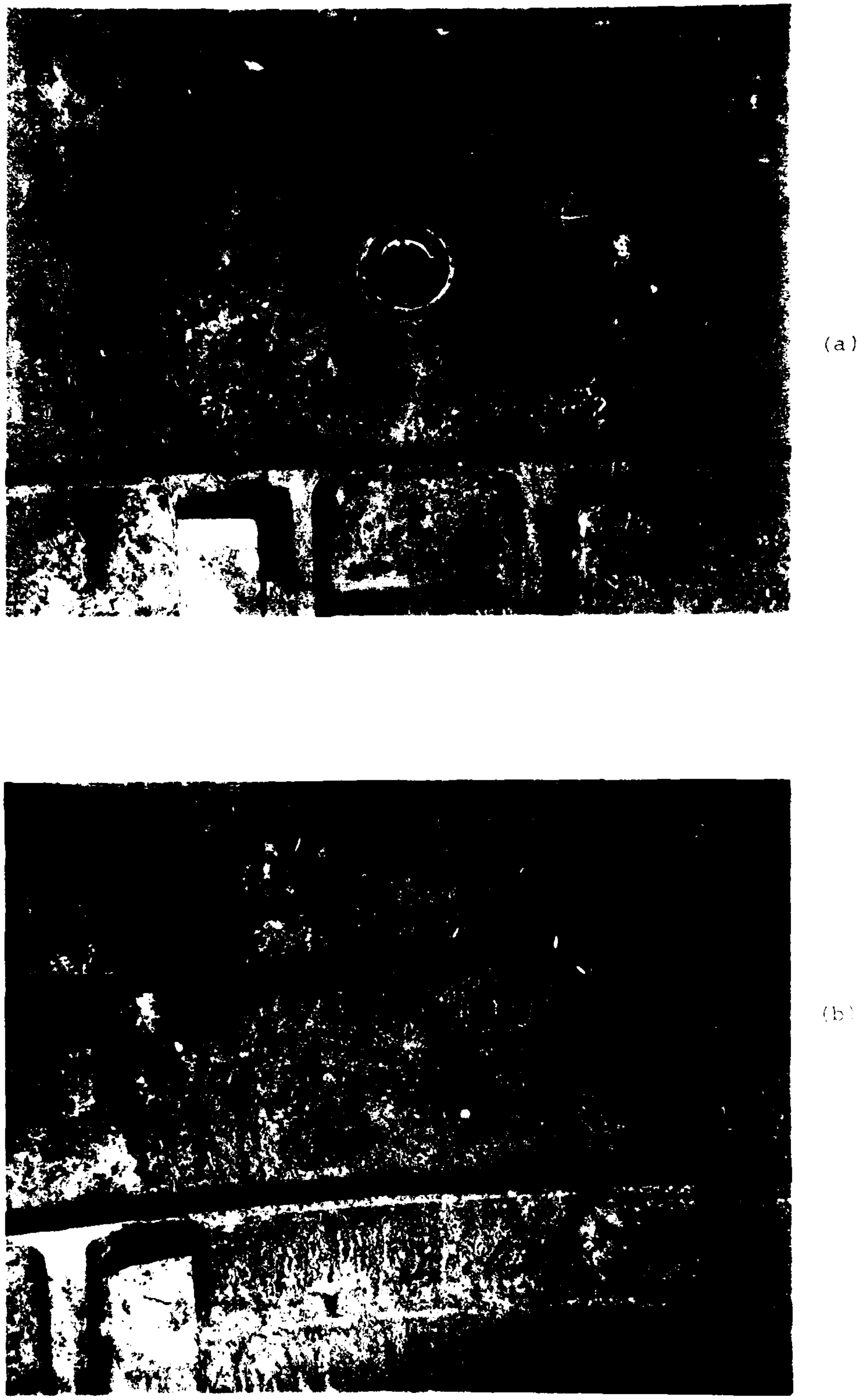


FIG. 4 Photographs taken within a closed, partially-used pot illustrating the influence of a protruding outlet on the flow pattern. The flow is from left to right. (b) illustrates more clearly the pattern on the right of the outlet.

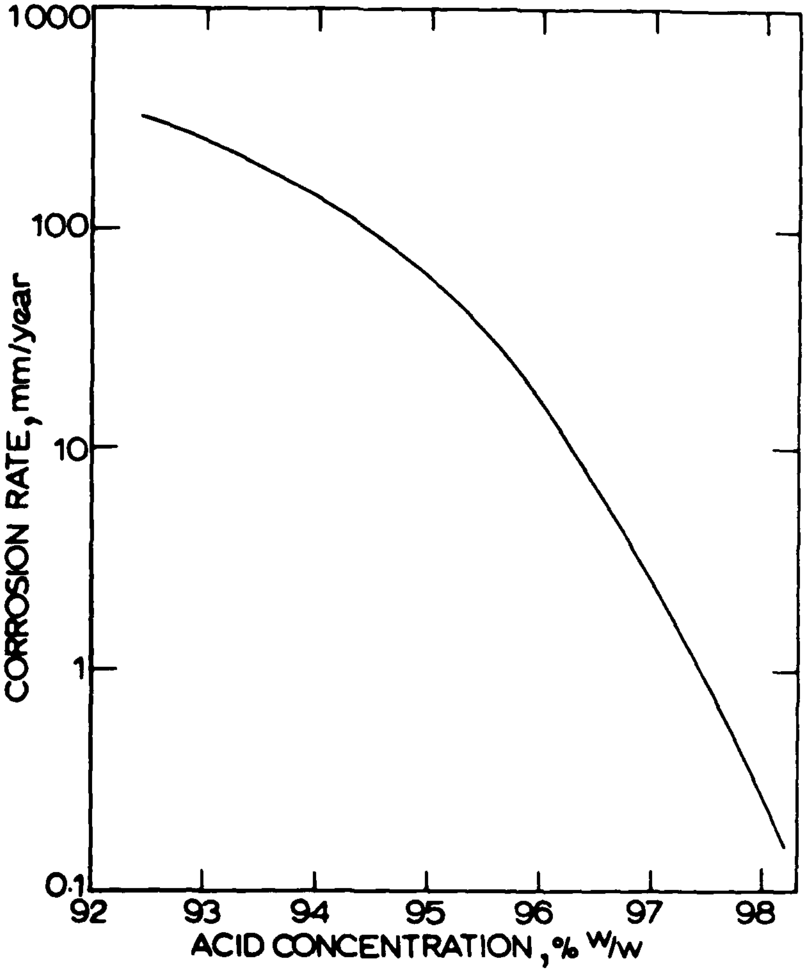


FIG. 5 Graph of the variation of corrosion rate of cast iron in boiling concentrated sulphuric acid plotted against the acid strength [21].

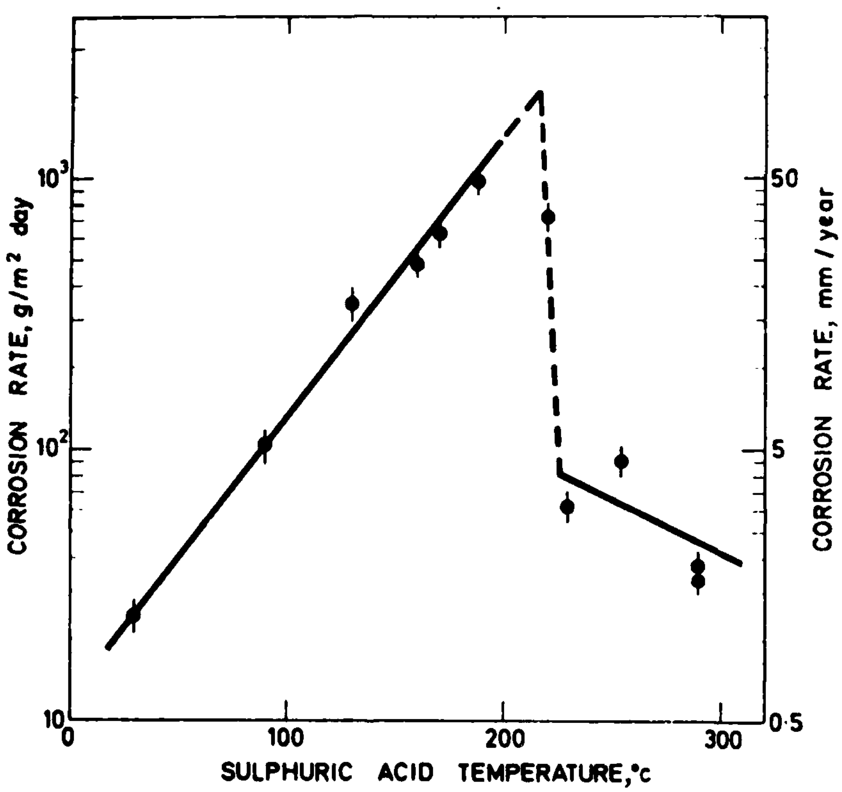


FIG. 6 Graph of the corrosion rate of cast iron in 96% sulphuric acid plotted against temperature [18].

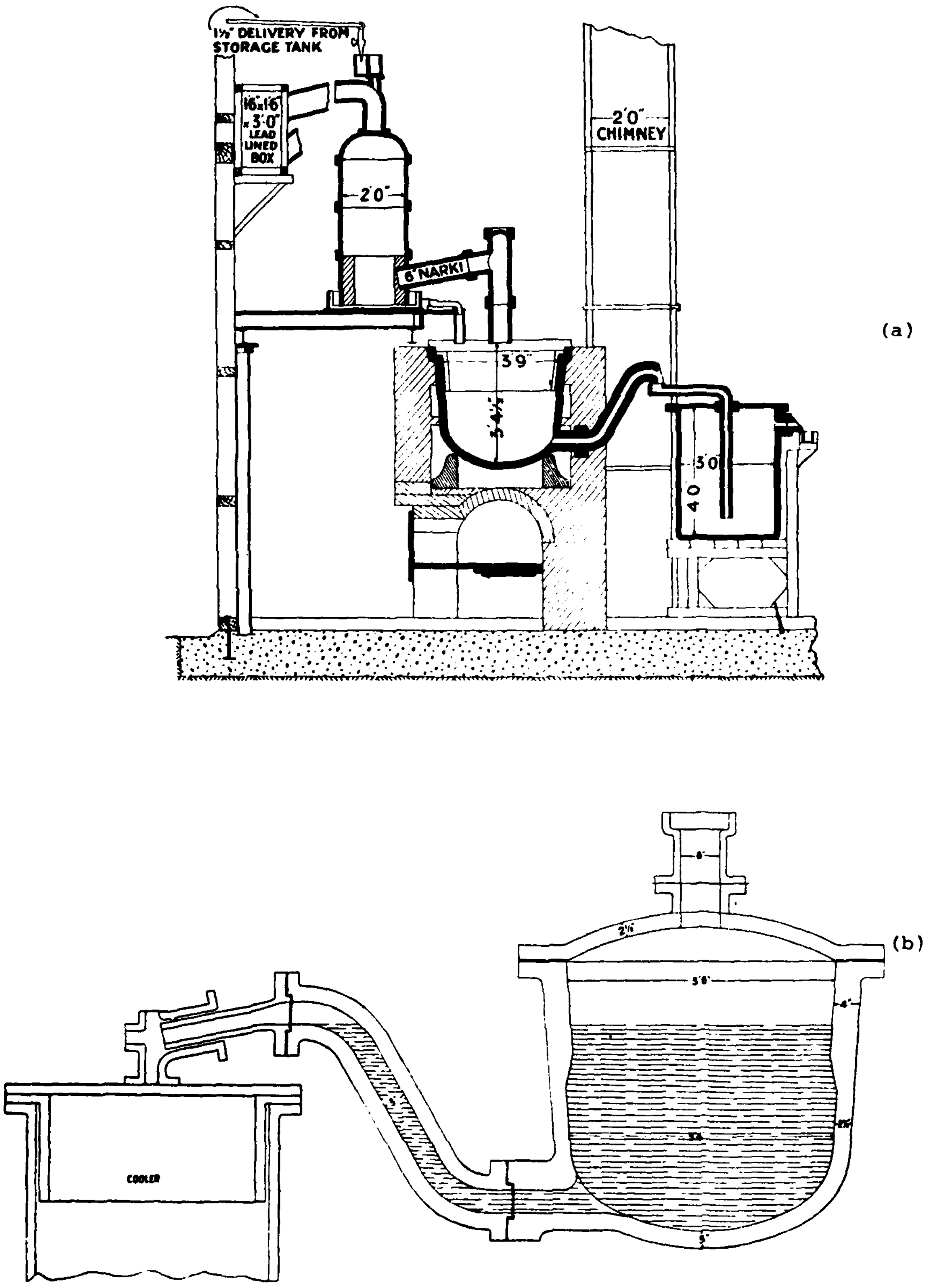


FIG. 7 Cast iron concentrating pots of the Dreyfus type, erected in 1916 to increase the strength of the sulphuric acid from 93% to 96.5% H_2SO_4. In (b) the wall thickness at the acid surface line has been increased to four inches [1].

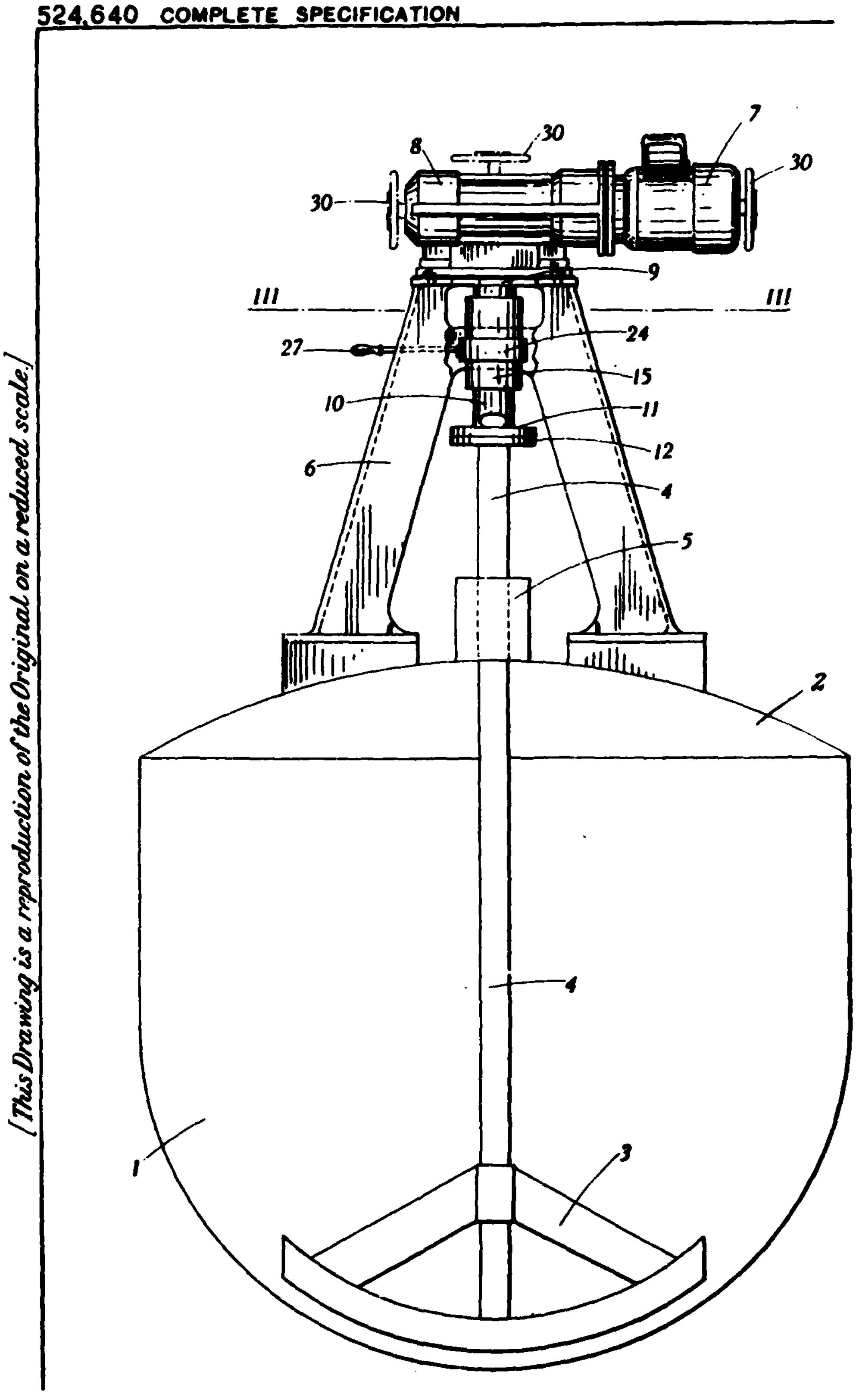


FIG. 8 Bamag rotary stirring device [6].

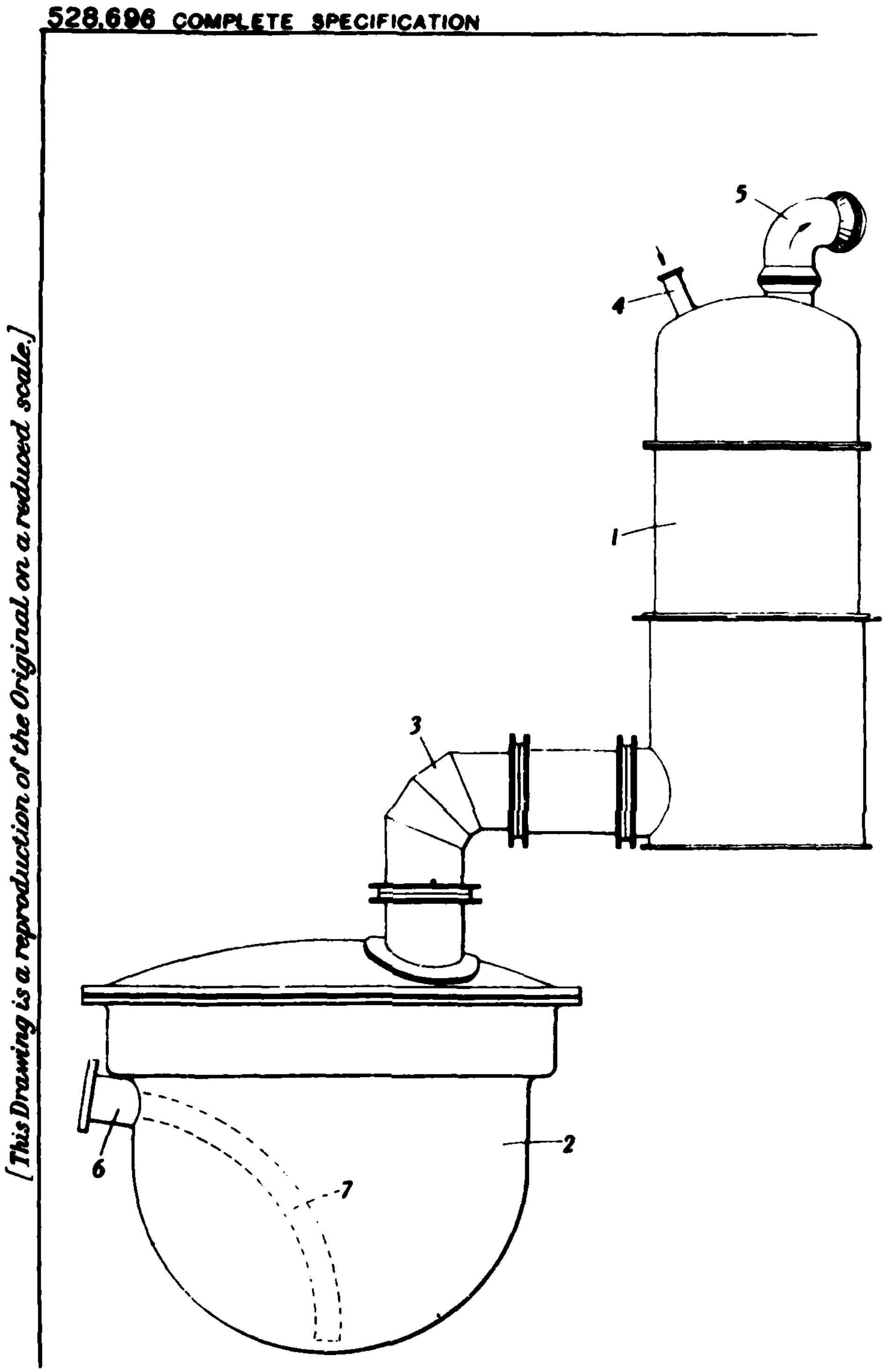


FIG. 9 Bamag acid concentration plant [7]. Note the siphon-type dip pipe for the overflowinq of the concentrated acid.

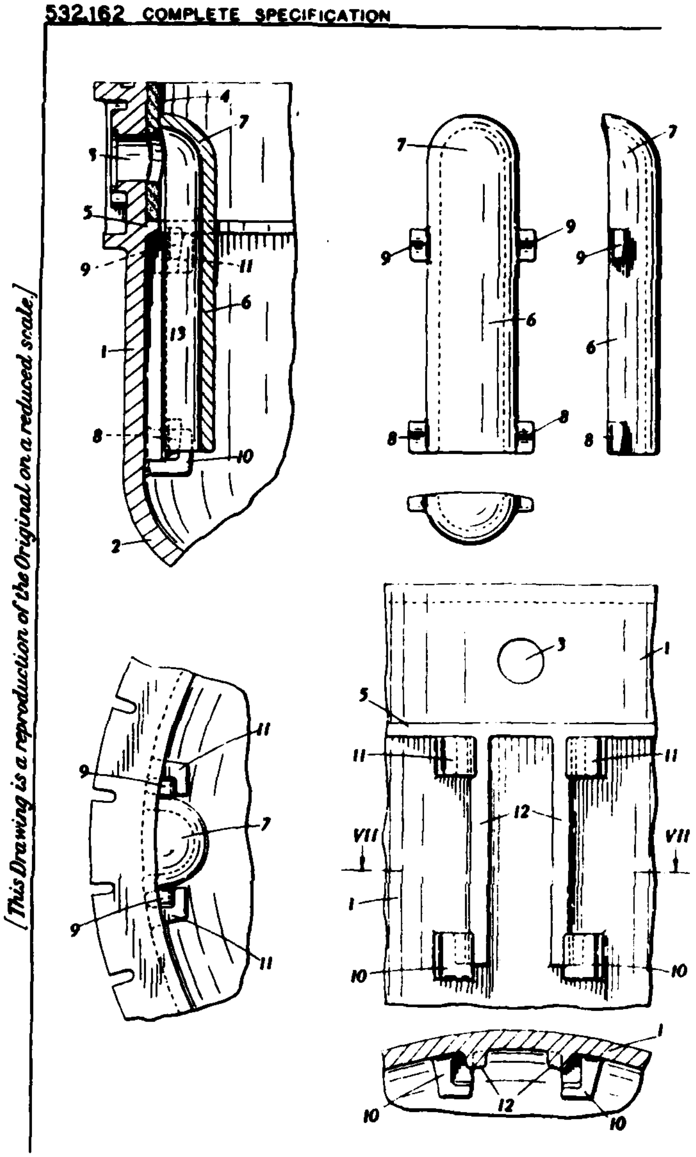


FIG. 10 Bamag cowl [8] that is used to create a substantially closed passage for concentrated liquid from the lower parts of the still to the outlet aperture. The numbers on this figure indicate the following:

1,	the vertical wall of the still.
2,	the still bottom wall.
3,	outlet aperture for concentrated liquid.
4,	internal protective ring of tiling.
5,	circumferential ledge on the wall to support tiling.
6,	removable cowl disposed over the outlet aperture.
7,	part-spherical cowl-like portion of 6.
8 and 9,	two pairs of lugs.
10 and 11,	corresponding pairs of L-brackets for the lugs.
12,	two vertical extending ridges.
13,	closed passage extending from near the bottom of the still to the outlet aperture.

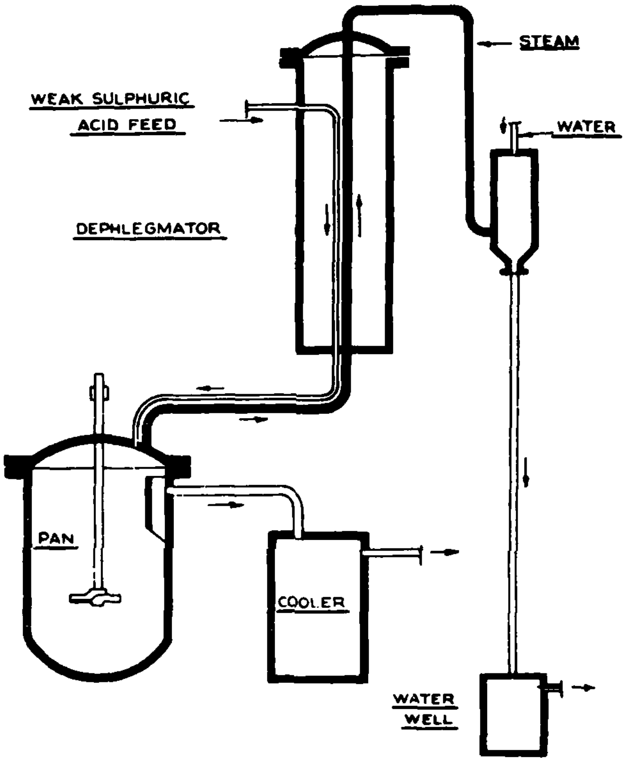
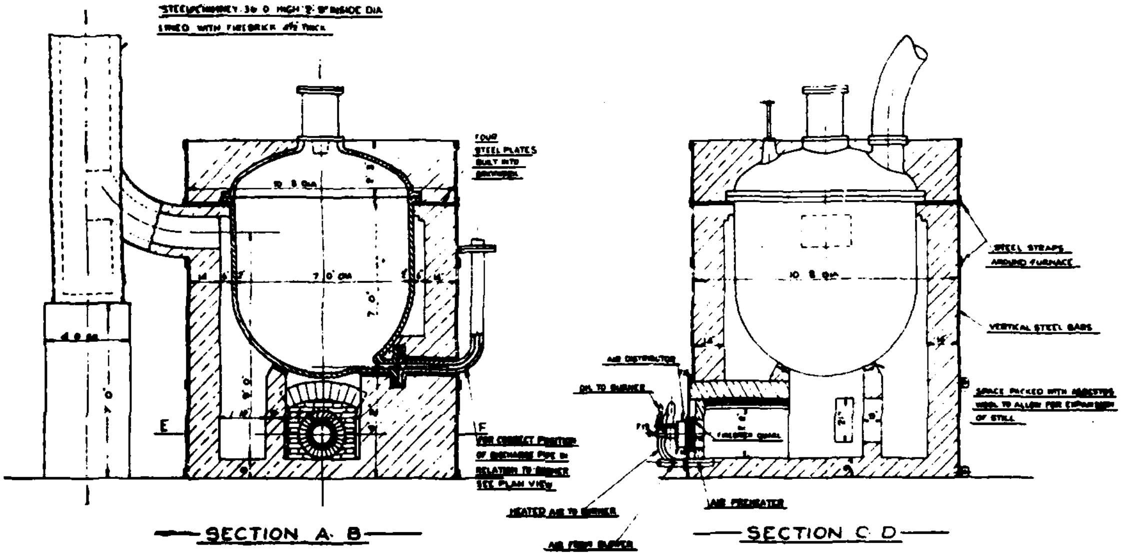


FIG. 11 Diagrammatic sketch of cast iron pot dephlegmator concentrator [9]. Note the cover over the concentrated acid outlet.



SECTION A-B

SECTION C-D

FIG. 12 Cast iron pot with external outlet (swan-neck type) [9].

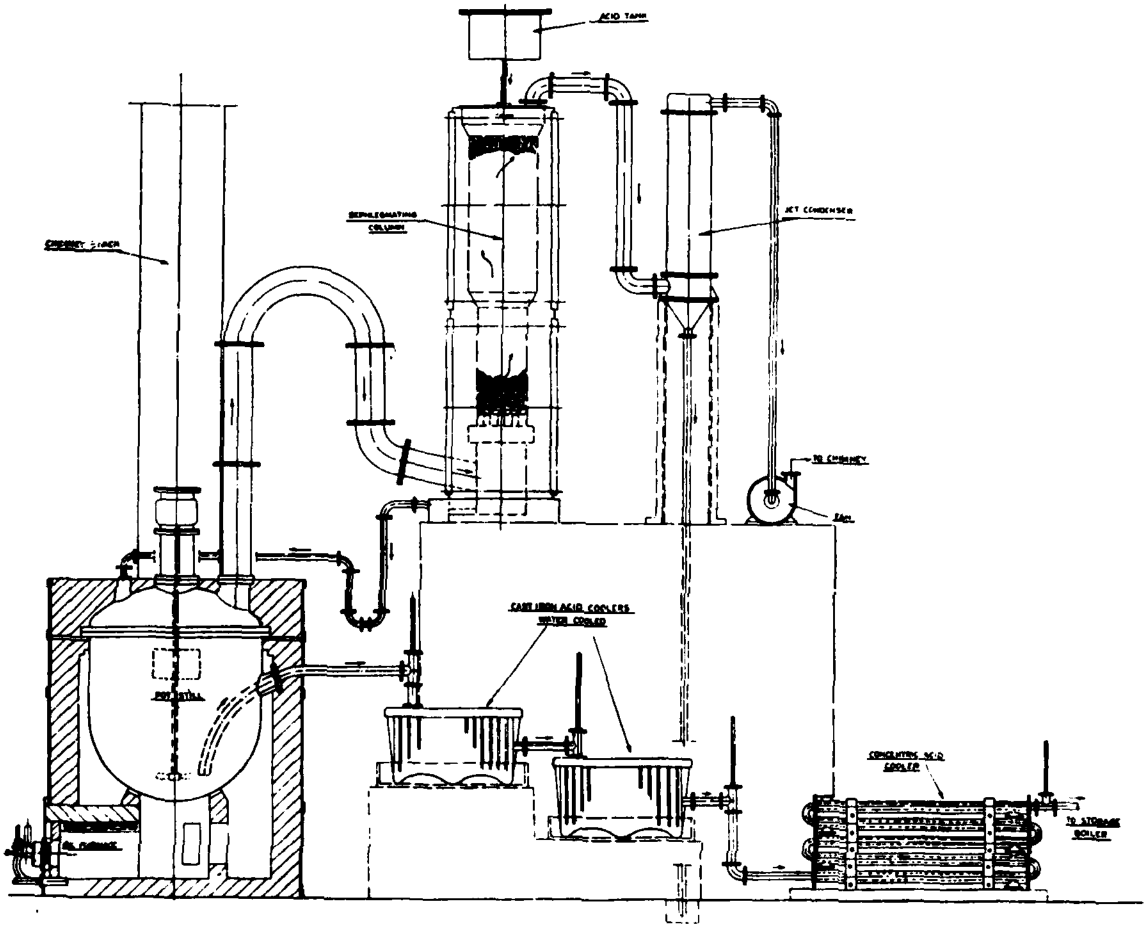


FIG. 13 Diagrammatic layout of complete acid concentrating plant [9]. Note in particular the internally-arranged concentrated acid outlet and its relative position to the weak acid inlet.

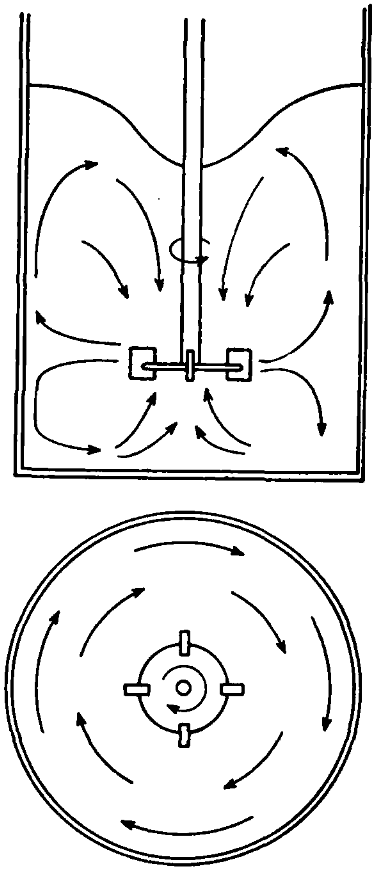


FIG. 14 Flow pattern with impeller mixer illustrating the three velocity components and vortex formation [30].

FIG. 15 A used cast iron Bamag pot incorporating a cowl. The gap at the top of the cowl clearly indicates that the cowl was intended to be used with some sort of internal protective wall cover.

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