THE DESIGN OF PLANTS FOR HANDLING HYDROFLUORIC ACID

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SUMMARY

The paper discusses the special problems in the design of process plant for handling hydrofluoric acid. Standards of containment superior to those normally applied to industrial acid uses are not required but such standards are difficult to achieve because of corrosion problems. Caution is necessary in using corrosion data obtained from the literature and welding can present problems.

Introduction

In recent years the use of fluorine derivatives has increased considerably. Until lately, when elemental fluorine has become available, this has generally involved the use of hydrofluoric acid.

The first large scale use in a modern process outside the metallurgical industries was the Phillips alkylation process. This came into prominence during the war, and because of the state of emergency a considerable amount of data was released.[1] This data still forms the most useful source for essentially anhydrous systems in the presence of organic materials.

The useful properties of uranium tetrafluoride and hexafluoride has inevitably resulted in these compounds playing a fundamental part in nuclear fuel processing. Their production has entailed high temperature processing with hydrofluoric acid, fluorine, and other fluorinating agents. The present paper is concerned with the use of hydrofluoric acid in this field.

Hazards Associated with Hydrofluoric Acid

Hydrogen fluoride (HF) both in the anhydrous state and in solution in water is a very reactive chemical. It is not, however, particularly prone to reactions of explosive violence.

The hazards in handling hydrogen fluoride are associated with its toxicity and its ability to produce severe burns. Containment is therefore the primary problem, and this is made more difficult by its corrosive nature.

Anhydrous hydrogen fluoride boils at 19·54°C at atmospheric pressure and, in consequence, reactions at moderate temperatures utilising the liquid phase require pressurised equipment. Its low heat of vaporisation, *circa* 1950 cal/mole for pressures above atmospheric, makes it possible that large volumes of vapour will be released in the event of a burst in a pressurised system. This problem reduces rapidly in magnitude as the concentration in aqueous systems is reduced to that of the azeotrope at 37·5% HF, boiling at 112·4°C at atmospheric pressure.

The toxicity of hydrogen fluoride is evidenced both in direct effects and to a lesser extent in the long term effects of fluorides generally. Breathing hydrogen fluoride vapour causes pain and damage to the respiratory system ; breathing of small amounts of very dilute gas for a short period is unpleasant and possibly painful, but is not likely to cause permanent damage.

Table I represents conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day without adverse effects. The values are time-weighted average concentrations over a normal working day. Values for a number of gases are shown in the table for comparison.

TABLE I.—*Exposure Threshold Limit Values*

Gas	p.p.m.	mg/m³	Ref.
HF	3		2
Fluoride/Dust	—	2·5	2
F	0·1		2
HCl	5		2
Cl	1		2
HCN	10		2
SO_2	10		3
SO_3	2		3

It has been found that hydrogen fluoride vapour can be detected by most people in concentrations as low as 2 p.p.m. by its smell. At levels of 60 p.p.m. the vapour is intolerably irritant on breathing, and concentrations of 50–250 p.p.m. cause damage to the lungs. As a design figure, therefore, 10 p.p.m. should be regarded as a maximum for brief exposure in an emergency.

Fluorosis resulting from inhalation of fluoride dusts is a form of sclerosis (stiffening) of the bones due to fixation of calcium, and takes some years to develop. The risk of fluorosis from hydrogen fluoride is considered slight, but of course any plant handling hydrogen fluoride is also likely to be handling fluorides and the problem must be taken into account.

Contact of liquid hydrogen fluoride with the skin causes burns which are very painful and can cause serious permanent damage to the tissue. The wounds are exceptionally slow in healing.

Acid of over 60% strength will cause immediate apparent damage and pain, but in the case of contact with acid below 20% strength the appearance and pain may be delayed for some hours. Contact with the eyes is particularly dangerous and can cause blindness.

Corrosion in Systems Containing Liquid Hydrogen Fluoride

The available corrosion data for hydrogen fluoride has now grown to considerable proportions, but much of it refers to

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particular conditions and is not widely applicable. Many of the reported data have been obtained in tests of short duration and this casts considerable doubt on their significance ; great care must be exercised in their application. The additional data presented in this paper are also restricted in their use, but it is hoped that by defining the conditions an additional relevance may be given them.

The data concerned in this section of the paper have been obtained for the design and from the operation of the hydrofluorination reactors and the hydrogen fluoride rectifying unit attached to the experimental fluidised bed unit for the production of uranium tetrafluoride at Springfields. It is therefore relevant to consider the flow diagram of the plant shown in Fig. 1.

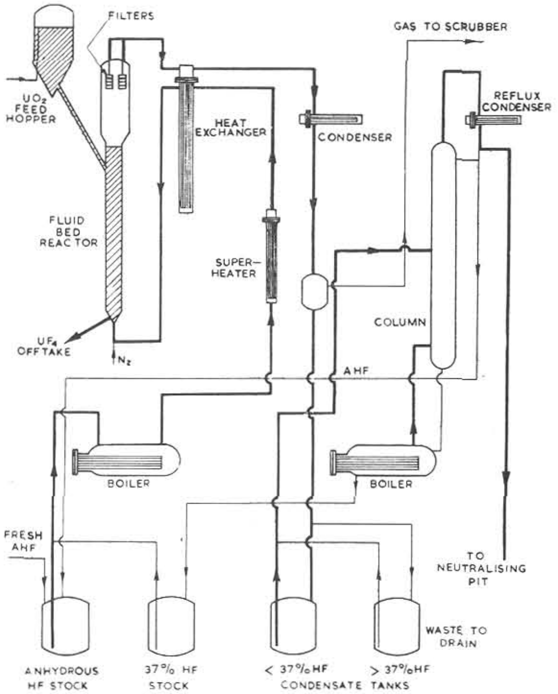


Fig. 1.—*Production of uranium tetrafluoride*

The process has been described in detail by Hawthorn, Shortis, and Lloyd.[4] Uranium tetrafluoride is obtained by decomposing uranyl nitrate to uranium trioxide, followed by reduction with hydrogen to uranium dioxide, which is then converted to uranium tetrafluoride with hydrofluoric acid gas in a fluidised bed reactor.

$$UO_2+4HF \rightarrow UF_4+2H_2O$$

The reaction is currently carried out batchwise at temperatures between 200 and 450°C giving a tail gas varying in composition from 0% HF at the beginning of the reaction to 100% HF at the end.

Hydrogen fluoride vapour is generated in a boiler and after passing through a superheater and heat exchanger, is used to fluidise the bed of uranium dioxide, with nitrogen being added as required. The tail gases leaving the bed pass through filters and the heat exchanger before passing to a condenser which removes water and residual hydrogen fluoride. The condensate is segregated into hydrogen fluoride above and below the azeotrope strength.

The hydrogen fluoride is recovered in a simple rectifying plant, hydrogen fluoride of azeotrope strength being recovered from the still bottoms and either water or anhydrous hydrogen fluoride from the column top, depending on whether the feed was below or above azeotrope concentration. The recovered azeotrope may be used to feed the reactors during the early part of the reaction.

The generally accepted materials of construction for plants handling liquid hydrogen fluoride of concentrations greater than 75% are Monel and carbon steel. The latter gives satisfactory resistance in the cold and may in some cases be more economical than Monel for hot hydrogen fluoride. For concentrations lower than this Monel and copper have given satisfactory performance in different plants. Stainless steels in general are unsatisfactory for all concentrations.

Silver is also a satisfactory material of construction for hydrogen fluoride plants and possesses superior resistance in the presence of oxygen and oxidising agents. Magnesium alloys are also resistant to hydrogen fluoride under slightly oxidising conditions, but their use is yet undeveloped. Trials are being carried out with Magnox, the fuel element canning alloy.

The corrosion rates of all these materials are considerably influenced by the presence of air, oxidising agents, agitation, and trace amounts of other materials. Recent work on the re-processing of zirconium and stainless-steel clad nuclear fuels has involved the use of strong oxidising agents with dilute hydrogen fluoride, to dissolve these alloys. No truly resistant material has been found, but alloys such as Monel have given moderate resistance in the presence of nitric acid and chromates. Carpenter 20 and some stainless steels have also given reasonable performance provided welds are avoided. For use with hydrogen peroxide/hydrogen fluoride solutions, Hastelloy C shows some resistance. The anhydrous system NO_2/HF is resisted adequately by Monel.

For the Springfields plant it was decided to use Monel for parts handling liquid hydrogen fluoride except for the storage of cold anhydrous acid where carbon steel was used. A number of straightforward corrosion tests were carried out and the results are shown in Table II.

TABLE II.—*Laboratory Tests on Monel Specimens in Boiling* 40% *Hydrofluoric Acid* (130°C) *with a Hydrogen Blanket*

Vol % O_2 in purge gas	Penetration rate (mm/yr)	
	Liquid	Vapour
0	0·29	0·027
0·1	0·54	0·048
1·0	1·92	0·30
Air Blanket	0·55	25·6

The specimens included radiographed argon arc welds with Monel 60 wire and no preferential attack was noticed on the welds.

Design was based on oxygen contents of less than 0·1% in gas streams.

It has been reported in the literature that Monel is easy to weld and that since it is a solid solution type alloy the welds are homogeneous. In practice considerable difficulty in producing sound welds has been experienced during the construction of the Springfields Plant.

The standards decided on were virtually the same as had been used successfully with stainless steel on the Windscale plants. These are rather more stringent than Lloyds Class I. It was soon found that the technique had to be considerably different.

For plates thicker than $\frac{1}{4}$ in. it was found that metal arc welding with fluxed Monel 130 or 140 electrodes gave satisfactory results. For thinner plates the best results were obtained by forming an internal bead run made with an argon arc torch using unfluxed Monel 60 electrodes, the weld then being filled with metal arc 130 or 140 electrodes. Attempts to carry out the initial run by fusing the plates with argon arc produced highly porous welds. Careful weld preparation and absolute cleanliness had to be observed during welding.

The vessels were not designed for full radiography, although butt welds were used where it was possible without undue expense.

TABLE III.—*Monel Piping—Specification U.K.A.E.A.(I.G.)* 70591. *Material to B.S.* 1532, *fully annealed*

Bore (in.)	Outside dia. (in.)	Wall Thickness s.w.g.	Wall Thickness (in.)
1	$1\frac{11}{32}$	14	·080
2	$2\frac{3}{8}$	12	·104
3	$3\frac{1}{2}$	10	·128
4	$4\frac{1}{2}$	—	·250

The piping used is thin-wall to U.K.A.E.A. standard (see Table III). This was found to be very difficult to weld. The most satisfactory technique found was argon arc welding with Monel 60 wire. It was found essential to radiograph the welds since bad porosity could occur in welds which had no unacceptable visual defects. Fig. 2 shows an extreme example of this kind of porosity. Approximately 80% of the early welds which passed visual inspection were later rejected on radiographic examination, although with increasing practice the percentage of faulty welds has now been reduced to normal proportions. Careful weld preparation and absolute cleanliness are even more important than in the case of plate, and it was found essential to exclude air draughts which could temporarily deflect the argon shielding.

The corrosion experienced on the plant during initial operations is indicated by the results in Table IV.

The results covered in the table can be divided into three periods during which operating conditions were different, particularly with respect to the oxygen content of the process gases.

Fig. 2.—*Section through an argon arc/Monel 60 electric weld showing serious porosity with no external or internal visuals defects—1 in. N.B. pipe*

During period I the plant was being frequently shut down for mechanical checks, thus allowing ingress of air and occasional oxygen contents as high as 5%. It was found in practice that the oxygen content did not fall below 0·1%. The corrosion rates experienced during this period were in line with the rates determined in the laboratory tests as in Table II, when allowance is made for the variable oxygen content. It was therefore decided to introduce hydrogen into the feed gas

TABLE IV.—*Plant Corrosion Rates*

Specimens suspended in plant

Unit	Period	Approximate acid strength	Temperature T°C	Oxygen content	Exposure Time At T°C (h)	Exposure Time Total (h)	Mean Corrosion Rate Penetration (mm/yr.) Liquid At T°C	Liquid Total	Vapour At T°C	Vapour Total
Boiler	I	40%–80%	80°C–150°C	0·1–0·5%	656	762	1·4	1·2	2·7	2·4
	II	40%–80%	80°C–150°C	100 ppm	—	450	—	10	—	10
	III	40%–80%	80°C–150°C	<100 ppm	39	226	8·0	1·4	1·2	0·2
Boiler	I	80%–100%	50°C–80°C	0·1–0·5%	129	241	0·24	0·13	0·3	0·16
	II	80%–100%	50°C–80°C	100 ppm	428	543	0·05	0·04	0·08	0·06
	III	80%–100%	50°C–80°C	<100 ppm	1248	1393	0·09	0·08	0·06	0·05
Boiler	I	40%–80%	50°C–112°C	0·1–0·5%	570	770	0·4	0·3	0·8	0·6
	II	—	—	—	—	—	—	—	—	—
	III	40%–80%	50°C–112°C	<100 ppm	292	1080	0·5	0·13	0·6	0·16
Condensers :	I	10%–100%	80°C–150°C	0·1–0·5%	—	277	—	1·4	—	—
Inlet ..	III	10%–100%	80°C–150°C	<100 ppm	—	330	—	0·6	—	—
Outlet ..	I	—	20°C	0·1–0·5%	—	400	—	—	—	0·33
Distillation : Column										
Top ..	I	100%	20°C	0·1–0·5%	—	230	—	0·6	—	—
Bottom ..	I	38%	112°C	0·1–0·5%	—	230	—	2·2	—	—
Heat exchanger :										
Shell ..	I	70%–100%	Approx 200°C	0·1–0·5%	—	420	—	—	—	0·1
Tube ..	I	70%–100%	Approx 200°C	0·1–0·5%	—		—	—	—	0·4
Superheater ..	I	70%–100%	190°C	0·1–0·5%	—	970	—	—	—	0·4
	I	100%	190°C	0·1–0·5%	—	129	—	—	—	0·1

to the reactor to reduce the oxygen level. This was successful and combined with less opening up of the plant enabled levels of 100 p.p.m. to be maintained continuously during period II. It was therefore somewhat surprising that the corrosion rates increased in some vessels as high as 10 mm/yr. during this second period.

Results in the third period have generally been similar and the oxygen content was further reduced to less than 100 p.p.m.

Despite the evidence from the initial corrosion tests that no preferential attack occurred at welds, a number of welds failed in practice in the course of all the periods and it was evident that some preferential attack on welds was taking place. It should be emphasised that some of the corrosion rates experienced were sufficient to account approximately for a number of failures in thin-walled piping, but the fact that the failures were, with few exceptions, associated with welds, made it desirable to investigate weld corrosion further.

A careful examination of the radiographs taken at the time of welding showed that a number of welds which subsequently failed had marginal defects. It was also found that the list of failed welds contained rather more cases where, in order to secure a sound weld, cutting and re-welding had been required. A corrosion programme on welded specimens was therefore begun, this being carried out in more refined apparatus which had been developed during the course of the corrosion programme. This apparatus gave extremely accurate control of the oxygen content and adequate stirring ; additionally, extreme care was taken in the preparation of the samples, these being cut from the middle of plates of a thickness appropriate to the type of weld being tested. Tests were made on welds carried out by argon arc with Monel 60 filler, and with metal arc Monel 130 and 140 electrodes. Initial results indicate that the Monel 130 weld is cathodic compared with parent metal, whereas Monel 60 is slightly attacked preferentially to parent metal, and Monel 140 is attacked more severely. Figs. 3 and 4 show samples. It is yet too early to say whether the cathodic form of the 130 weld results in undercutting of the weld, although there is no sign of this to date.

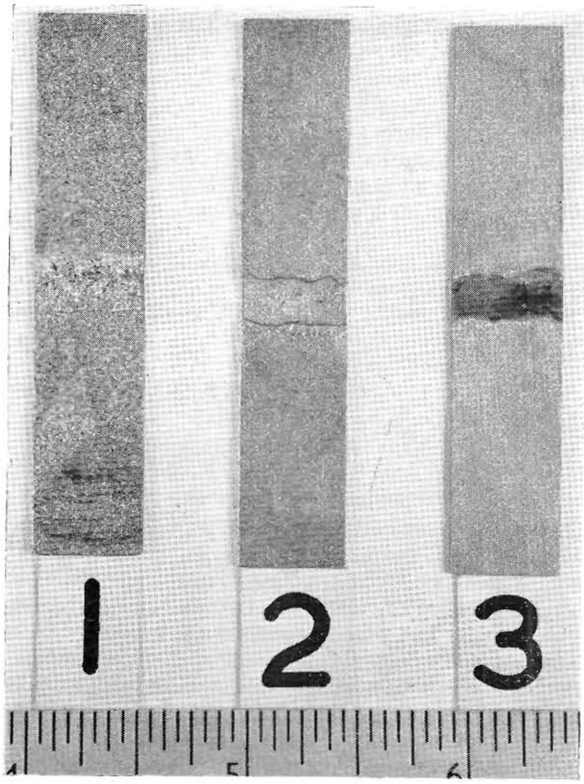
Further work has indicated that undercutting of the weld does not take place. Also included in the programme were a number of re-welds, but results are not yet available on their performance.

Not included in the tabulated data is the performance of Monel and Inconel in the reactor proper, which has been exposed to gaseous hydrogen fluoride at temperatures up to 450°C ; here the corrosion has been slight and performances is satisfactory.

It is noticeable that the severe corrosion is associated with intermediate strengths of liquid hydrogen fluoride at higher temperatures.

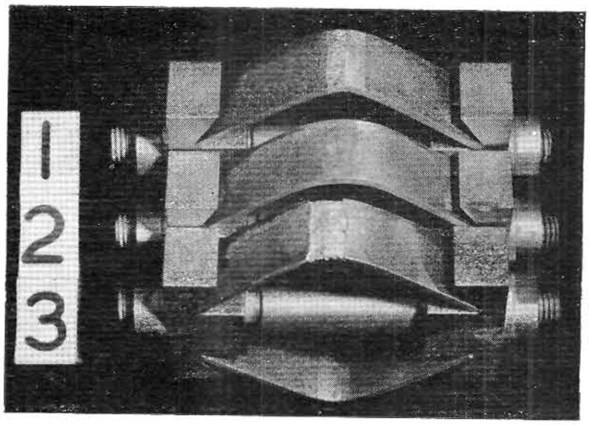
Increased corrosion rates have been experienced at the entrances to heat exchangers which are evidently due to the condensation of acid during the heat-up cycle, and severe pitting of tubes has resulted. Parts fabricated from bar-stock have suffered severe end-grain attack and this type of construction should be avoided.

Plainly, factors other than oxygen content affecting corrosion have entered into plant operation. Nitric acid has been found to be present in the recycled hydrofluoric acid at up to 20 p.p.m. and it would seem likely that higher levels might occur locally. Sulphuric acid is added to the uranyl nitrate entering the process and traces of sulphide and sulphate have been found in the recovered hydrofluoric acid. It is thought that the sulphate does not materially effect the corrosion, but testing is being carried out on the effect of small quantities



1 — argon arc/Monel 60 weld
2 — metal arc/Monel 140 weld
3 — metal arc/Monel 130 weld

Fig. 3.—*Liquid-phase corrosion of Monel welds (plan view) in 40% hydrogen fluoride at 70°C after 1000 hours exposure with 1% oxygen atmosphere*



1 — argon arc/Monel 60 weld
2 — metal arc/Monel 140 weld
3 — metal arc/Monel 130 weld

Fig. 4.—*Liquid-phase corrosion of stressed Monel welds in 40% hydrogen fluoride at 70°C after 1000 hours exposure with 1% oxygen atmosphere*

of nitric acid. The present results indicate that levels of 20 p.p.m. HNO_3 give only a moderate increase in the corrosion rate, but levels of 100 p.p.m. might cause increases of the same order as experienced in some sections of the plant. It is possible to postulate reasons for fluctuations in the nitric acid content which could cause the increase in corrosion between period I and period II.

Sulphide corrosion has definitely been experienced in the condensers, where deposits of essentially copper sulphide have been found on the tubes. It seems probable that the sulphide content of the gases is virtually completely removed here.

Design Considerations

It has been shown that hydrogen fluoride is not intrinsically more toxic than many other industrial chemicals, and that provided an equivalent standard of containment can be established, hydrogen fluoride can be handled just as readily.

The first consideration in the design of any plant handling hydrogen fluoride is thus that of coping with corrosion. Much can be done in considering the basic process to be operated. If this can be arranged so that intermediate strengths of hydrogen fluoride, *i.e.* $<70\%$ and $>20\%$, are not handled, the problem is much simplified. If the reactions can be carried out in the vapour phase, well above the dew point, corrosion will again be much less.

When these points have been considered the effect of leaks on both plant operation and safety must be assessed.

If the amount of hydrogen fluoride that can be released from a failure is small and would not constitute a hazard away from the plant itself, it is reasonable to consider an open-type plant. This might arise in the case of small low pressure plants with low liquid hold-up. In general, however, if the corrosion conditions to be expected are severe, *e.g.*, as might arise with intermediate strength acid, the amount of maintenance work will be high and in this country an enclosed plant may be necessary. The same enclosure may be utilised to contain any leaks which may occur since in general, maintenance of this type of plant is not practicable during operation.

The enclosed cells must be adequately ventilated to a scrubber capable of dealing with the largest leak likely to occur.

Air changes should be such that with minor leaks, maintenance workers can enter without air lines ; in these circumstances the air entering the scrubber will be below breathing tolerance and hence will be virtually free of hydrogen fluoride on leaving. Under major leak conditions, however, the scrubber should be capable of reducing the concentration of hydrogen fluoride to 10 p.p.m., thus ensuring that there is no hazard to surrounding areas.

In both open and enclosed plants the operation should be remotely controlled from control rooms supplied with fresh air. In open plants, stop-valve operation would be direct, but all valves and flanges should be shielded as a protection against acid spray ; this precaution is also advisable to protect maintenance personnel in an enclosed plant. Entry into open plants inevitably involves a clothing change as must entry into the cell area of an enclosed plant ; it is therefore an advantage in an enclosed plant to have as many of the manual valves as possible operated by means of extension spindles through the enclosure walls.

In designing both open and enclosed plants rather more care than usual should be devoted to providing easy and safe exits. Platforms should have wide passage ways and exits at each end ; in the case of cells, doors should be provided at each end leading to external stairways, duplicated internally where desirable. As far as possible cells should be similar in layout so that in the event of a leak personnel will have no hesitation in taking the correct way out.

The usual provisions for emergency treatment equipment must be made with warm water showers, eyewash bottles, etc., at regular stations.

Sprays have been installed in the cells of the Springfields plant, so that a major leak could be killed quickly, and to ensure that any pockets of acid accumulated on platforms, steelwork, etc., have been thoroughly diluted and washed down. Without this precaution it could be hazardous to enter a cell after a major leak.

An important feature of both process and plant design must be the elimination of oxidising agents and dissolved oxygen. If this can be achieved the corrosion problem becomes reasonable. Inert gas blanketing is therefore essential, nitrogen being commonly used for this purpose.

A consequence of this is that processes should be continuous. The large changes in composition associated with batch processes make the control of corrosion difficult and the similar changes in the amounts of material in vessels make the control of oxygen contents difficult even though inert gas blanketing is practised.

For anhydrous hydrogen fluoride carbon steel is the natural choice with Monel being used where there is possibility of dilution to 70% or where temperatures are above about 50°C. For cold dilute and intermediate strengths of hydrogen fluoride polythene and polypropylene should be given serious consideration. It is probable that hard rubber, neoprene, and butyl rubber would also be satisfactory for this service.

For hot intermediate strengths the choice is between Monel, silver, and magnesium alloys. The particular conditions of the process to be used will determine this choice. In the case of Springfields plant it is not yet possible to say which is the most economic. In both cases the design of equipment should be of the simplest ; in the case of Monel this is to reduce the number of welds and make it possible to radiograph them all ; in the case of silver to facilitate lining.

It can be seen that all factors affecting corrosion come into the fundamental decision as to whether to have an enclosed or an open plant.

Although an enclosed plant is considerably more expensive, it is reasonable to consider that where enclosure is necessary this extra cost is merely a reflection on the state of development of the process and has its compensations in reducing the operating costs of such under-developed processes. Thus a highly-refined continuous process with small in-process hold-ups, and one that avoids the more corrosive conditions and hence can be as safely built as an open plant, is likely to have a small operating staff and a high on-stream time ; by contrast, a less well-developed batch-process with large hold-ups and severe corrosion problems will have a much larger operating staff. Under the latter conditions the savings in process labour due to elimination of change times and the ability to go on operating the plant in safety with quite considerable leaks can obviously lead to economies to offset the cost of enclosing the plant.

For both types of plant a high standard of construction is essential for economic as well as safety reasons. The tendency of Monel to give porous welds undetectable by visual inspection demands the highest standards of radiographic inspection.

Mechanical Design

It has already been mentioned that design of vessels should be simple and, if in Monel, should be capable of radiographic inspection. Vessels holding liquid and, in particular, stock tanks, should not have bottom outlets.

The attachment of branches to vessels is difficult and should be avoided if possible by the use of alternative designs, *e.g.* coils rather than tubular heat exchangers with headers.

Fillet welds have not been eliminated in the Springfields plant, but care has been taken to provide full penetration welds with a reinforcing plate.

An alternative preparation which could be considered is that shown in Fig. 5. This has been used extensively on stainless steel at Windscale and can be satisfactorily radiographed.

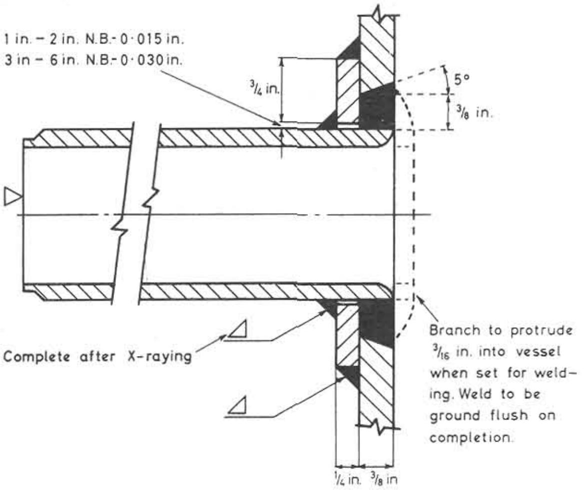


Fig. 5.—*Branch weld preparation*

Forged weld-neck flanges should be used exclusively.

Allowance should be made in the design of vessels for accelerated corrosion rates. Thus at the Springfields plant the vessels were designed for a test pressure of 250 lb/in^{2}g and a working pressure of 100 lb/in^{2}g with an additional allowance of corrosion at the anticipated rate of 0·5 mm/yr.

Since the actual working pressure is 50 lb/in^{2}g, an adequate margin for accelerated corrosion between inspection periods has been obtained.

Piping should be designed to eliminate as many welds as possible and should be fully radiographed. Corrosion with hydrogen fluoride is reportedly velocity-sensitive,[1] and hence pipes should be of ample bore.

Forgings should be used for flanges, valves, and other fittings since sand castings in Monel have proved very porous and have almost all been failures.

Where carbon steel fittings are used with anhydrous hydrogen fluoride, the use of Monel trim is advisable.

Three satisfactory methods of flange jointing have been found in the Springfields plant, but others would certainly work.

Because of the high temperatures at the reactor, a metallic joint was chosen and Monel and Inconel lens rings have proved satisfactory. These were subsequently used throughout the experimental plant. The importance of using rings of the same composition as the parent flange metal must be emphasised. Severe electrolytic corrosion takes place in the presence of liquid hydrogen fluoride if slightly dissimilar metals are used.

Spiral packings of interleaved Monel and P.T.F.E. trapped between flat flange faces have also proved satisfactory up to 200°C.

For low temperature service P.T.F.E.-enveloped asbestos packings have been proved suitable.

Whilst there is no fundamental objection to the use of glanded pumps in hydrogen fluoride service, Springfields experience is not encouraging. Carbon has not proved successful as a rubbing contact in hydrogen fluoride and it is consequently difficult to find a suitable pair of rubbing surfaces for mechanical seals on pumps. Work is still continuing on this.

P.T.F.E. is not in general a suitable gland packing for high-speed shafts and consequently the simple type of centrifugal is not used at Springfields.

Double diaphragm pumps are used for boiler feeds; a glandless extended-spindle centrifugal is being developed at the Capenhurst laboratories which should prove a more satisfactory long-term answer.

Air-operated control valves used at Springfields have bellows seals made from Monel with a P.T.F.E. laminated safety packing. The bellows have been subject to stress corrosion, and since they are inevitably thin, their life has been short. The edge-welded type of bellows which is the most satisfactory in stainless steel is less so in Monel for hydrogen fluoride service since the metal is attacked adjacent to the welds: the convoluted type is preferable. At Springfields many of these valves are located on filter blow-back units of the fluidised bed and here the corrosion has been substantially reduced by heating the bellows to ensure that condensation cannot take place.

Safety valves are protected by bursting discs. Careful location of these can usually ensure reasonable replacement times.

Operational Experience at Springfields

The experimental plant from which experience has so far been gained has been built with reactors in an existing building and the boilers and hydrogen fluoride recovery plant in an adjacent open structure. The reactors are the core of the process and most of the effort has been expended on these. Since the reaction is at high temperature, they are constructed of Inconel and no substantial corrosion problems have been met. In consequence of the development programme on the reactors, most of the experience in hydrogen fluoride handling has come from the boiler and feed systems, these having operated both on azeotrope concentrations and on high strength hydrogen fluoride and the condensation systems which have operated at all concentrations.

It has been found anew that even a small proportion of failures can cause serious disruption to a programme; however, with experience it has been found possible to tolerate small leaks.

Fairly extensive arrangements for detecting leaks were installed but they proved unnecessary. The nose is far more sensitive and specific. Small leaks have been adequately dealt with by hosing with water and neutralising with soda ash. The visible fume from a leak serves as an adequate warning to plant personnel.

Repairs by patching leaky welds have proved totally unprofitable and it has in general proved better to insert a new piece of pipe with the welds located in convenient positions. Decontamination of the plant for repairs has proved remarkably easy. For low strengths of hydrogen fluoride, washing out with water is adequate. For anhydrous hydrogen fluoride, where water cannot be used, draining followed by nitrogen purging removes the hydrogen fluoride rapidly. The times taken to do this in vessels are naturally longer, but the process is effective.

Experience gained in the use of protective clothing confirms that of other users. In control rooms and other non-contact areas normal plant overalls are used. For any inspections and valve operation in the plant area, *i.e.* that portion which in the new plant will be in the cells, operators wear face shields and gloves in addition to normal overalls. In the event of a suspected or known leak of considerable magnitude operators entering the cell wear a polythene suit with hood and self-air mask. Fitters are similarly clad for emergency maintenance, *e.g.* to tighten a leaking valve gland with the plant under pressure. Fitters also wear a polythene suit, hood and self-air mask when starting to strip down plant which has been purged. As soon as it has been ascertained that no pockets of hydrogen fluoride remain, they revert to normal overalls, eye-shields and gloves.

The amount of maintenance possible with the plant on-stream has grown with experience. Control valves positioned between isolating valves and fitted with a manual by-pass are now replaced without shut-down or purging, fitters using the clothing described above. In general those maintenance operations involving a small release of hydrogen fluoride can be safely completed.

Conclusions

The toxicity of hydrogen fluoride is comparable to that of many other industrial gases, but its burning effect, in liquid form, is more severe than that of most acids. It can readily be detected by smell at its safe working exposure-level and leaks of all but dilute acid are readily located visually by the fume.

In consequence, the design of safe plant does not require standards of containment in excess of those normally applied to industrial processes using acids. The measures required to achieve satisfactory containment are functions of the process design and state of development. With present knowledge, plants handling large volumes of hydrogen fluoride at its boiling point under moderate pressures should have secondary containment cells if there is any possibility of high corrosion rates.

Confidence gained from operations at Springfields indicates that further plants could be built in the open with suitable modifications to the larger hold-up vessels and with the improvements expected in the process.

Corrosion rates of Monel and Inconel by gaseous hydrogen fluoride of all concentrations are low at temperatures above the dew point, and plant design does not present new problems. Corrosion rates of Monel by liquid anhydrous hydrogen fluoride are low, but are accelerated in the presence of small quantities of oxidising agents, but even so they are still tolerable and do not present severe problems. Intermediate strengths of hydrogen fluoride give reasonable corrosion rates, but in the presence of small amounts of oxidising agents the rates increase rapidly and become severe. Operating experience indicates that under plant conditions the rates can be accelerated further.

Caution should be exercised in the use of corrosion data on Monel from the literature : much of this data is on tests of inadequate duration.

Satisfactory welding of Monel is difficult. For thin-wall piping, argon arc welding with Monel 60 electrodes is the most satisfactory method and for plate, metal-arc with Monel 130 electrodes. Monel plants demand high standards of construction, and design should be such as to allow for radiographic inspection of welds both in vessels and pipework. Failure to do this is likely to result in a plant with exorbitant maintenance costs and doubtful safety.

Careful attention to detail design is required since there are few satisfactory solutions to problems of sealing static and moving joints. Operating experience shows that reasonable flexibility in the toleration of small leaks is practicable provided that first-aid measures are taken and personnel are correctly clothed.

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