

SANDVIK SANICRO 28

A HIGH-ALLOY SPECIAL STEEL FOR HEAT EXCHANGERS IN PHOSPHORIC ACID PLANTS

by

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SUMMARY

In cases where metallic materials are used in heat exchanger for the concentration of phosphoric acid, they have often proved to have an unsatisfactory service life. The experiments which have been made with higher alloy steels have not been successful, partly because corrosion resistance has not always been good enough and also because these steel have been too expensive. Today, therefore, the phosphoric acid industry extensively uses graphite heat exchangers, which have hitherto been judged the best alternative, despite the inferior mechanical properties of graphite. As a better alternative to graphite SANDVIK has developed a new high alloy stainless special steel called SANDVIK Sanicro 28 with the following analysis: max 0.020% C, 27% Cr, 31% Ni, 3.5% Mo, 1.5% Cu. Sanicro 28 combines the following properties:

- good corrosion resistance
- good fabrication properties
- good mechanical properties

Compared with graphite, Sanicro 28 offers the following advantages, among others:

- no risk of cracks resulting from mechanical and thermal stresses
- higher acid flow rates permissible, which means lower scaling rates and more efficient heat transfer
- more efficient cleaning methods can be used
- simple and inexpensive heat exchanger designs are feasible.

Compared with existing metallic materials, Sanicro 28 offers the following advantages, among others:

- much longer service life, thanks to superior corrosion resistance
- the possibility of using phosphate rock of higher impurity content
- no risk for intercrystalline corrosion in connection with welding.

THE PRODUCTION OF PHOSPHORIC ACID

Practically all new phosphoric acid plants employ what is known as the wet process, and there is unlikely to be any shift in favour of the dry process, considering the differences in the investment costs and energy consumption which the two processes involve.

During the past ten years, a large number of processes have been developed to overcome the basic limitations of the so-called classical dihydrate process, which however, in modified form, still remains one of the dominant methods.

In the classical dihydrate process, the attack on the phosphate rock takes place at such temperatures and at such concentrations of P_2O_5 that the calcium sulphate which is formed crystallises as dihydrate, $CaSO_4 \cdot 2H_2O$. Figure 1 shows the temperature ranges and the P_2O_5 concentrations within which the three different forms of calcium sulphate are formed. In practice there is no distinct boundary between the various crystalline forms, and a combination of operating conditions therefore has to be chosen which comes well within one of the ranges defined in the chart, in order to ensure uniform hydration. This is necessary in order to maintain the reproducible

filterability of the calcium sulphate.

The hemihydrate process, which operates at far higher temperatures, is more difficult to control than the dihydrate process and has not been used in full scale operations for any great length of time. Great attention, however, has been aroused by the advantages claimed for this process, namely product acid of higher concentration and purity.

For almost ten years now a number of phosphoric acid plants have been in operation which combine the two processes. The most successful processes are based on dihydrate-hemihydrate crystallisation with intermediate separation by centrifuging. Recrystallisation of the dihydrate to hemihydrate is followed by a filtration process. Last of all, the product acid which has a concentration of 33-35% P_2O_5 is concentrated.

Figure 2 is a flow chart for the Central-Prayon (dihydrate-hemihydrate) process. The greatest advantages of this process are a high yield (98-99% P_2O_5) and the quality of calcium sulphate which is suitable for further upgrading. The drawbacks include greater complexity and somewhat heavier investment costs. The ultimate choice of process is normally settled after the evaluation of a host of different factors. At present the classical dihydrate process predominates together with processes also including a hemihydrate stage. On the other hand, the purely hemihydrate processes have not yet gained any appreciable share of the market. One can safely assume that throughout the foreseeable future the great majority of new phosphoric acid plants will also include a concentration unit.

CONCENTRATION

Systems for the concentration of filtered acid may differ somewhat, but their underlying principles are usually much the same. Filtered acid, at a concentration of 28-35% P_2O_5 depending on the process used, is heated indirectly with steam, usually in tube heat exchangers, and then vacuum pumped to a flash vessel, where volatile gases such as SiF_4 evaporate together with the water. Figure 3 shows the design of a forced circulation evaporator used for concentrating phosphoric acid. The concentration unit may include one, two or three of these evaporator stages.

The heat exchanger is the part of the concentration unit which is exposed to the severest operating conditions and therefore demands most maintenance. Heat transfer through the tubes gives an elevated surface temperature on the acid side, which in turn aggravates corrosive conditions and increases the tendency for salts, especially calcium sulphate, to be precipitated onto the tubes. Graphite tube and block heat exchangers have to a great extent solved the problems of corrosion, but the use of graphite, a material characterised by low strength and brittleness, is liable to result in sudden tube failures. The rapid changes of temperature which can occur in connection with shutting down or starting up often cause extensive tube fractures.

The use of graphite heat exchangers has not had any effect of the problem of scaling and the attendant need for regular cleaning. On the other hand certain improvements have resulted from changes in operating conditions and process monitoring. There are also other heat exchanger designs presenting advantages in terms of descaling and, above all, cleaning. One example of the latter type is given in figure 4, which shows a heating element of the kind used in Prayon's concentration system. The advantage of

this system is that individual elements can be removed for cleaning without the entire heat exchanger having to be taken out of operation.

The pulp and paper industry is faced with similar problems in connection with the deposition of calcium sulphate in evaporator plants. For a long time now, high pressure flushing has been used to clean these heat exchanger tubes, which are generally of the AISI 304 grade. The results of this method have been consistently very good, provided that sufficiently high pressure is used; 500 bar has proved to be the minimum requirement for efficient cleaning. Since the deposits are similar in nature, a corresponding pressure is presumably needed for the efficient cleaning of heat exchangers and tubing in phosphoric acid plants as well.

The feasibility of flushing at sufficient pressure, however, is limited by the poor mechanical properties of graphite. A metallic material does not suffer from any such limitations. A high acid flow rate has also been found to reduce scaling tendencies. Here again a limitation is imposed by the poor mechanical strength of graphite, since a higher flow rate also means greater pressure and wider fluctuations of pressure.

The ideal tube for a heat exchanger is therefore a metallic tube with good corrosion resistance and good mechanical properties and presenting a finished heat exchanger area which will be no more expensive or if anything cheaper than graphite.

Experience with Sanicro 28 to date, both in laboratory tests and in practical operation, has shown that Sanicro 28 measures up to these requirements.

THE EFFECT OF IMPURITIES ON THE CORROSIVENESS OF PHOSPHORIC ACID

Pure phosphoric acid is less corrosive than the stronger acids sulphuric acid and hydrochloric acid. As a rule, the standard grades AISI 316 and 317 are sufficiently corrosion resistant to be used as construction materials in pure phosphoric acid. But phosphoric acid produced by the wet method invariably contains such impurities as Cl^- , F^- , H_2SO_4 , Si^{4+} , Al^{3+} , Fe^{3+} , Ca^{2+} , Mg^{2+} in quantities depending on the type of phosphate rock used and on the concentration of acid. Moreover there are also solid constituents, mostly in the form of gypsum $\text{CaSO}_4 \cdot \text{XH}_2\text{O}$. Types and magnitudes of impurities occurring in phosphate, filter acid and concentrated acid have been summarized in Table 1.

The most corrosive impurity elements are Cl^- and F^- . These two elements have different effects on the resistance of the material. Cl^- , which has a large ionic radius, is weakly solvated and can therefore be adsorbed on the surface of the metal. This inhibits the passivation process which is the process responsible for the corrosion resistance of stainless steels. Cl^- in concentrated phosphoric acid is complex bound to only a slight extent by metallic ions.

The opposite applies to F^- , which has a small ionic radius. F^- forms strong complexes with many metallic ions, especially Si^{4+} and Al^{3+} . The complexes formed are SiF_6^{2-} , AlF_6^{3-} , AlF_5^{2-} , AlF_4^{3-} , AlF_3 .

Since non-complex bound F^- greatly increases the corrosion rate of a steel or nickel

alloy in the passive state and reduces the ability of the alloy to become passive, the presence of Si^{4+} and Al^{3+} is an advantage in terms of corrosion resistance. Corrosion rates of up to 1 mm/year can occur in certain materials in the passive state.

H_2SO_4 reduces pH, which is a disadvantage in terms of passivation and also affects the equilibria between F^- and Si^{4+} , Al^{3+} in various directions. Fe occurs almost entirely in the form of Fe^{3+} and therefore contributes strongly to the total cathodic process, i.e. the oxidizing capacity of the acid. Fe is therefore positive in terms of corrosion. Complex formation between Fe^{3+} and F^- is very limited. As far as is known, Mg^{2+} does not significantly affect corrosiveness.

THE EFFECT OF ACID CONCENTRATIONS

The following equilibrium may appear at P_2O_5 concentrations exceeding about 54%:



This reduces the free F^- content and with it the corrosiveness of the acid. But increased acid concentration also has an indirect effect. In the process of concentration, F^- is evaporated as the highly volatile SiF_4 and the total F^- content is therefore reduced. Investigations have pointed out that the Cl^- content is reduced during concentration. Possibly Cl^- is emitted as HCl .

CORROSION STUDIES

Experimental

All the alloys examined were tested in the form of cold rolled and annealed plates measuring 50 x 20 x 4 mm and ground with 200 grit paper. Chemical compositions and quenching temperatures are given in table 2.

The corrosion studies were carried out in synthetic phosphoric acid. The base solution was 70% H_3PO_4 (48.3% P_2O_5) and 4% H_2SO_4 . The tests were conducted in teflon vessels fitted with teflon coolers. Activation with a Zn rod was consistently used. The testing time was 1 + 3 days. The results given are the average of double testing for the three-day period.

Results

Effect of F^-

Tests were carried out in the base solution but with 60 ppm Cl^- 0.6% Fe^{3+} and varying contents of F^- . The total F^- content may be presumed to be identical with the free F^- content, since Al^{3+} and Si^{4+} were not present and the formation of complexes between Fe^{3+} and F^- is negligible.

The results, illustrated in figure 5, show that whereas alloy A (20Cr25Ni4.5Mo1.5Cu), for example, is greatly affected by increased F^- content, Sanicro 28 displays less sensitivity and corrodes all the time in the passive state. Alloys B and C have very high corrosion rates. This the corrosion resistance of Sanicro 28 in solutions of high F^- content is substantially better than that of the other alloys included in the tests. This does not only apply in phosphoric acid.

Effect of Cl⁻

The test solution was the base solution with 0.5% F⁻, 0.45% Fe³⁺ and various Cl⁻ contents. The results are shown in figure 6.

Increased Cl⁻ content does not affect the corrosion rates in the passive state (represented by the horizontal parts of the graphs). On the other hand the passivation abilities of the steels are affected. Whereas alloys A, B and C will only tolerate relatively small Cl⁻ contents, Sanicro 28 can be used in acids with relatively high contents.

Combined effect of F⁻ and Cl⁻

To the base solution was added 0.45% Fe³⁺ and various Cl⁻ and F⁻ contents. The total F⁻ content is equal to the free F⁻ content. The results are illustrated in figure 7.

Figure 7 shows that the use of alloys A, B and C is limited to low Cl⁻ and F⁻ contents while Sanicro 28 can be used in acids with high contents of both F⁻ and Cl⁻.

Effect of Si⁴⁺ and Al³⁺

As stated previously, F⁻ forms strong complexes with Si⁴⁺ and Al³⁺. This reduces the free F⁻ content, i.e. the portion raising the corrosiveness of the acid. Table 3 shows how Al³⁺ and Si⁴⁺ affect corrosion rates.

Table 3. Effect of Al³⁺ and Si⁴⁺ on corrosion rates in 70% H₃PO₄, 4% H₂SO₄, 60 ppm Cl⁻ and 0.6% Fe³⁺ at 100°C.

As can be seen in Table 3, Al³⁺ and Si⁴⁺ reduce the negative effect of F⁻. Consequently Sanicro 28 has acceptable resistance even in extremely high total F⁻ contents, while alloys A and B develop very high corrosion rates.

Effect of temperature

As in many other environments, a rise in temperature impairs corrosion resistance in contaminated phosphoric acid.

Figure 8 shows how the corrosion rates of Sanicro 28 and alloys D and E vary in the passive state with temperature. It should be noted that the corrosion rates of these three alloys have been ranked according to their Cr contents.

Alloys C and B corrode actively at all temperature. Alloy A has probably corroded in both the active and passive states

CORROSIVENESS OF ACIDS FROM DIFFERENT PHOSPHATES

The results obtained from laboratory tests in phosphoric acid, some of which have been presented here, make it possible to grade the corrosiveness of acids from different phosphates with reference to the composition of the latter.

Corrosiveness grading of acids from different phosphates

Group	Corrosiveness	Phosphate
I	low	South Africa (Phalabourwa) Nauru Senegal (Taiba) Florida (Tampa, Pebble) Brazil (Avaxa)
II	medium	North Carolina Kola Morocco (Khourighba, Usufia) Tunisia (Gafsa) Togo
III	high	Spanish Sahara (BuCraa) Syria Jordan Israel Mexico

The phosphates within each group are more or less interchangeable without any notable changes of corrosiveness.

Phosphates from different groups can of course be mixed in such proportions as to keep the corrosiveness of the acid at a suitable level.

The laboratory tests and practical trials have shown that Sanicro 28 functions very well in acids made from phosphates in groups I and II. Sanicro 28 can also be expected to do well in acids extracted from mixtures of BuCraa phosphate and phosphates from groups I and II. Probably this also goes for acid derived solely from BuCraa phosphate. Phosphates from Jordan, Syria, Israel and Mexico have very high chloride contents, > 5000 ppm, and can therefore only be used in limited proportions.

DISCUSSION

Corrosion tests described here which have been carried out in phosphoric acid manufactured by the wet method have yielded the results summarized in table 4.

Thus the corrosiveness of the acid rises steeply with rising F^- and Cl^- contents but declines with rising contents of Si^{4+} and Al^{3+} due to the formation of complexes with F^- , and also with rising contents of Fe^{3+} , which increase the cathodic process and stimulate active-passive transition.

Cr is the most positive of the alloying elements because it reduces the corrosion rate in the passive state and also increases the ability of active-passive transition.

As in most other environments, Mo has a positive effect because it stimulates the active-passive transition.

Cu has also a slightly positive effect on the active-passive transition while Ni has no effect. The main function of nickel as an alloying element is to provide an austenitic structure.

Sanicro 28 has been given a composition providing it with a very good capacity for active-passive transition (high Cr, Mo, Cu content), at the same time as its corrosion rate in the passive state is very low (high Cr content). Sanicro 28 is therefore highly resistant to contaminated phosphoric acid, and this has been confirmed both by laboratory tests and by practical trials.

FABRICATION PROPERTIES

As a general rule, the use of metallic materials means far simpler designs and cheaper fabrication than are possible with graphite. Because graphite tubes and tube sheets are only available in certain sizes, this restricts the range of sizes available for individual heat exchangers. The same restriction applies to block heat exchangers made from graphite. Moreover the number of manufacturers of graphite heat exchangers is very limited, whereas practically all manufacturers of heat exchangers can construct heat exchangers using Sanicro 28 tubing.

One very important factor when comparing Sanicro 28 and the metallic tubes of grades corresponding to 20Cr25Ni4.5Mo1.5Cu which have been used so far is the greatly superior post-welding corrosion resistance of Sanicro 28. During welding part of the heat-affected zone (HAZ) acquires a temperature which is critical to the precipitation of grain boundary carbides. Depending on the time factor, and with it the degree of carbide precipitation, and also on the corrosive conditions to which the material is subsequently exposed, intercrystalline corrosion is liable to occur. Corrosion attacks in HAZ have been a serious problem in heating elements as per figure 4 made from 20Cr25Ni4.5Mo1.5Cu. This type of corrosion is also eliminated by the use of Sanicro 28, thanks to the much longer times needed for carbide precipitation; see the time-temperature-corrosion diagram in figure 9.

Sanicro 28 can be welded by conventional methods such as MMA, TIG and MIG. As suitable filler material is available.

ECONOMIC ASPECTS

While Sanicro 28 generally costs more per foot of tube than does graphite, the difference is slight enough to be more than offset by the difference in fabrication costs. Therefore, when measured in terms of square feet of finished heat exchange surface, Sanicro 28 is a competitive alternative to graphite.

Compared to other metallic materials, Sanicro 28 is approximately 25% more expensive than alloys of the 20Cr25Ni4.5Mo1.5Cu type. On the other hand, the substantially

greater corrosion resistance of Sanicro 28 makes it possible to reduce the wall thickness, thereby minimizing or completely offsetting the extra cost, while still providing the advantage of a longer service life.

When compared to other metallic materials which are currently being used, or considered for use in phosphoric or super phosphoric acid services, Sanicro 28 has been found to be either competitive (\$/Ft.) or somewhat lower in cost.

PRACTICAL EXPERIENCE WITH SANICRO 28

Prayon - Engis, Belgium

The first complete heating element (Prayon type, figure 4) was installed in this plant in June 1975. The operating conditions are as follows.

Phosphate Rock: Equal mixture of Kola and Togo

Acid Analysis: 50-54% P_2O_5
0.6-0.8% F^-
100-200 ppm Cl^-
1% Al_2O_3
1% Fe_2O_3
1.6% SO_3
0.1% SiO_2

Temperature: Shell side acid, approximately 185°F
Tube side steam, 248°F

Previous Experience: 20Cr 25Ni 4.5Mo 1.5Cu tubes began leaking after twelve months service. Repairs, by welding, extended their life by another 18 months.
Sanicro 28 tubes have now been in service (under heat transfer) for almost four years with no, or very limited repairs needed.

Boliden - Helsingborg, Sweden

This plant also uses the Prayon concentration system. Experience here is much the same as the Prayon plant. Sanicro 28 elements have been in service since March 1976, with only one problem having been reported (a weld failure attributed to an error made in fabrication).

Based upon an inspection made in November 1978, it was estimated that the tubes had at least two-three years of life left, before any repairing or replacement would be necessary. This equates to a life of approximately three times greater than the 20Cr 25Ni 4.5Mo 1.5Cu tubes previously used.

Through 1978, Kola-rock was the primary feed for this plant. Today, mainly Moroccan rock is used.

Triomf - Potoschefstroem, South Africa

Prayon concentration system. Had been using 20Cr 25Ni 4.5Mo 1.5 Cu elements for three years. In June 1978 they changed over to Sanicro 28. They primarily use Phalabowra-rock (similar to Kola).

Fosforico - Huelva, Spain

Prayon concentration system. Have historically used plate element of 20Cr 25Ni 4.5Mo 1.5Cu. In early 1978, they installed a test element (tubular) of Sanicro 28 and have since placed a duplicate order. Rocks being used are Moroccan, Senegal and Spanish Sahara.

Kemira - Nystad, Finland

This is a Dorr-Oliver plant, using a Swenson concentration system. In September 1977, ten tubes of Sanicro 28 (.98" O.D. X .079" x 20') were installed in an existing graphite heat exchanger.

To date, all tubes are in operation with no problems having been reported.

Togo and Florida rock are the primary feed for this plant.

In addition to the cases cited herein, we have data obtained from a test heat exchanger tubed entirely with Sanicro 28, which has been operating in a Florida phosphoric acid plant for five months. To allow for the inclusion of maximum data, this will be prepared as a supplement to this paper. Copies will be available to attendees at the meeting.

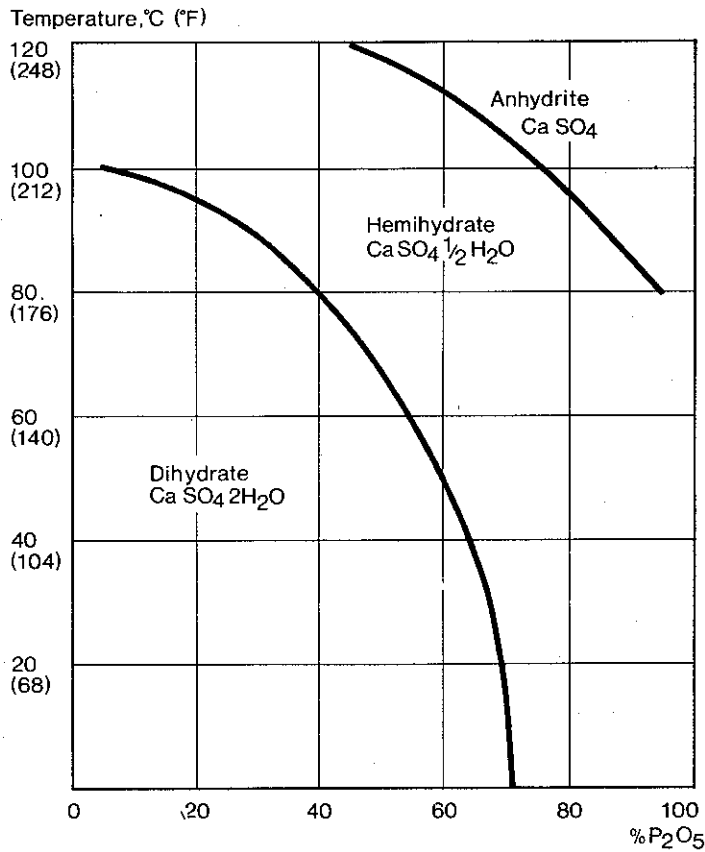


Figure 1 Phase diagram for the system
 $P_2O_5 - CaSO_4 - H_2O$

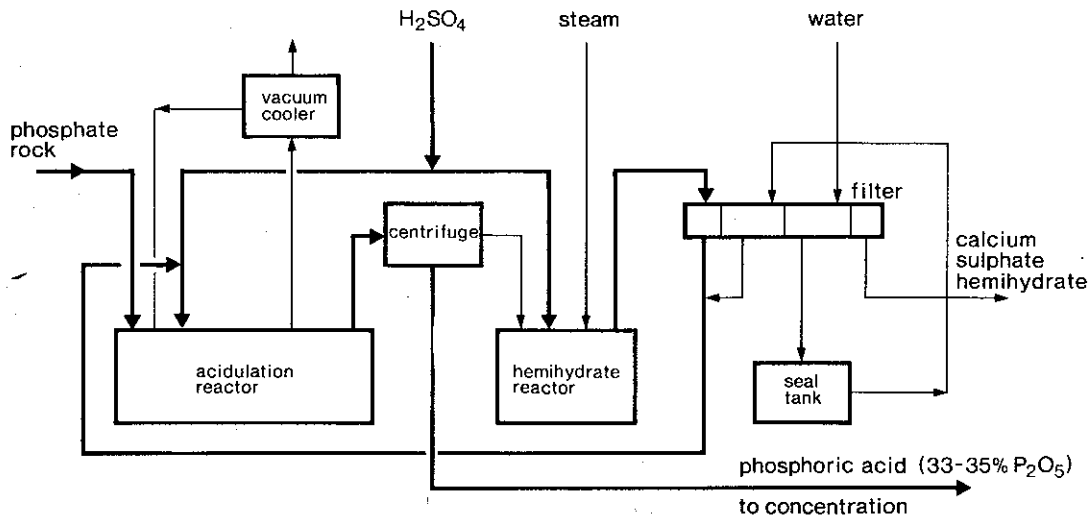


Figure 2 Flow chart for the Central-Prayon (dihydrate-hemihydrate) process.

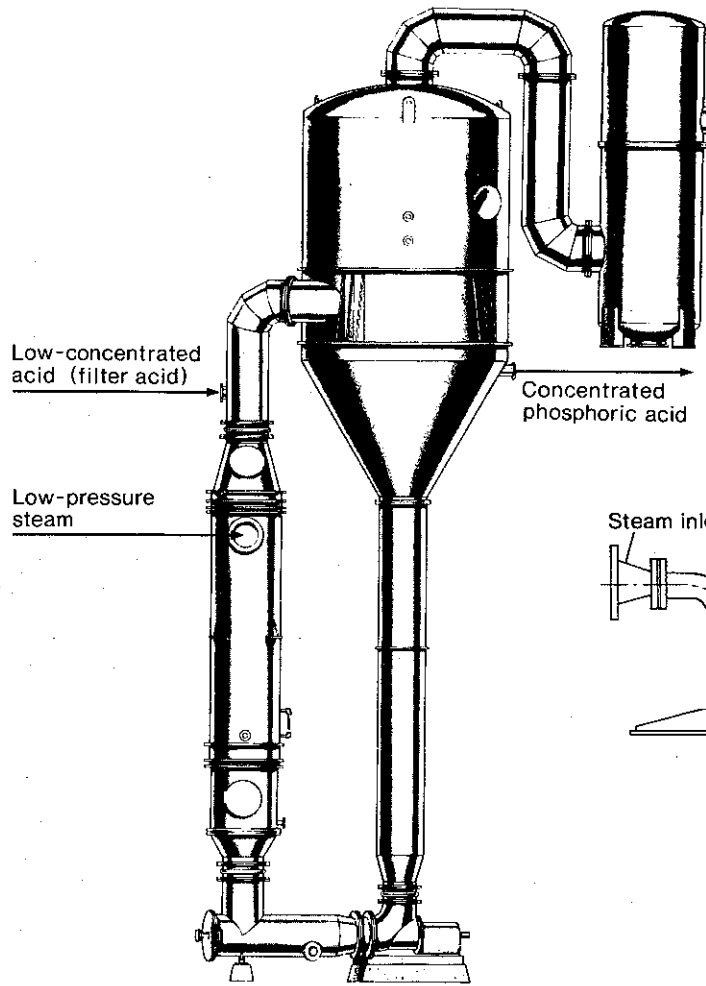


Figure 3 Forced circulation evaporator for the concentration of phosphoric acid

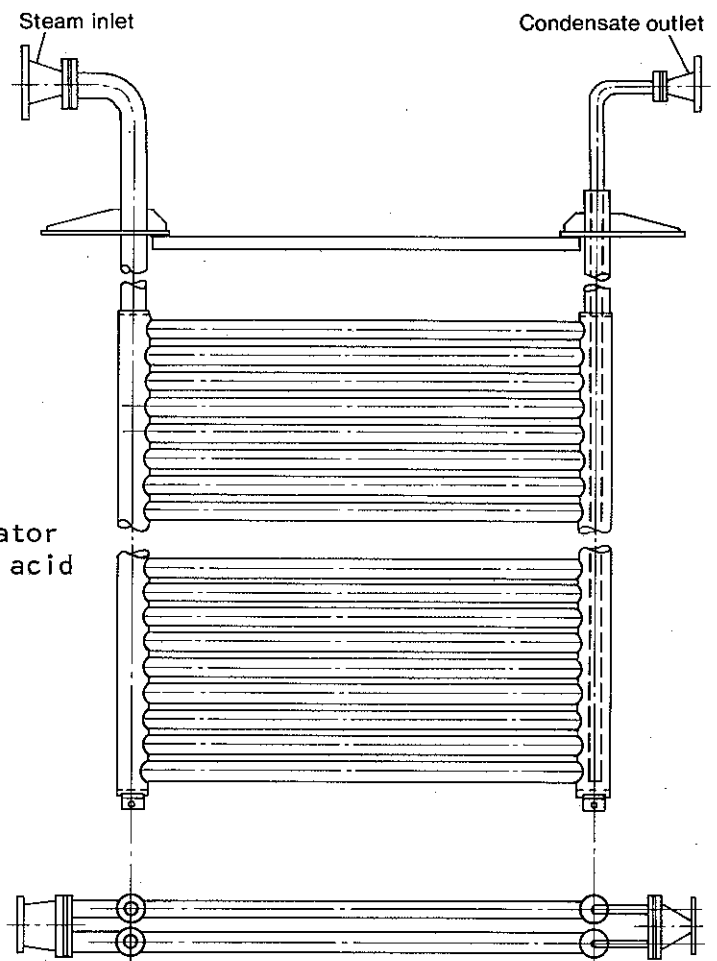


Figure 4 Heating element used in Prayon's concentration system.

Table 1. Impurities, % by weight

Impurity	Phosphate rock	Filter acid	Concentrated acid
SO ₃	0.15-4	1-4	1-4
H ₂ SO ₄			
F ⁻ *	2-4	0.2-3.5	0.1-1.5
Cl ⁻	0.02-1.0	0.005-0.1	0.002-0.05
SiO ₂ *	0.5-4	0.05-1.8	0.01-0.7
Al ₂ O ₃	0.2-3	0.2-3	0.2-3
Fe ₂ O ₃	0.2-3.5	0.2-3	0.1-2.5
MgO	0.1-1.8	0.1-1.5	0.1-1.5

* The American phosphate rocks normally have much higher fluoride and silicon dioxide contents, but the figures for filter acid and concentrated acid also apply to phosphoric acid derived from these ores. There are also minor deposits of phosphate in Syria and Israel, for example, with much higher chloride contents than those stated above.

Table 2. Chemical composition, %, and quenching temperature of the tested alloys

Grade	C	Si	Mn	P	S	Cr	Ni	Mo	Cu	Ti	Nb+Ta	W	Co	Quench. temp. °C
Sanicro 28	.015	.02	.17	.005	≤.003	26.0	30.6	3.55	1.04	-	-	-	-	1140
A	.013	.46	1.76	.007	≤.003	19.46	25.24	4.50	1.49	-	-	-	-	1100
B	.040	.34	.67	.026	≤.003	19.4	33.05	2.24	3.40	.05	0.43	-	-	1100
C	.017	.23	.53	.009	.002	20.8	41.4	3.08	1.68	.83	-	-	-	1050
D	.02	.34	1.35	.023	.006	21.87	45.3	6.35	1.79	-	2.43	-	-	1100
E	.010	.09	.60	.010	.004	15.8	55.9	16.0	.008	-	≤.02	4.6	1.6	1120

A = SANDVIK 2RK65
 B = Carpenter 20Cb3¹⁾
 C = Incoloy 825²⁾
 D = Hastelloy G³⁾
 E = Hastelloy C³⁾

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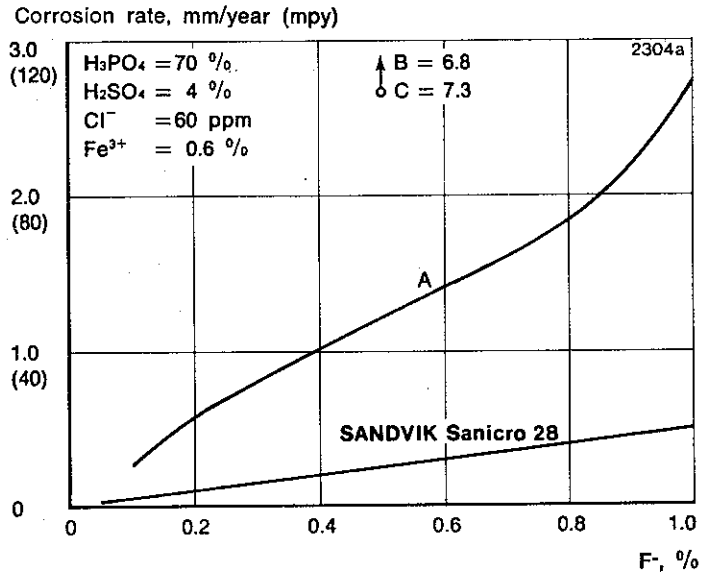


Figure 5 Influence of free fluoride content on the corrosion rates of Sanicro 28 and alloys A, B and C (Table 2).

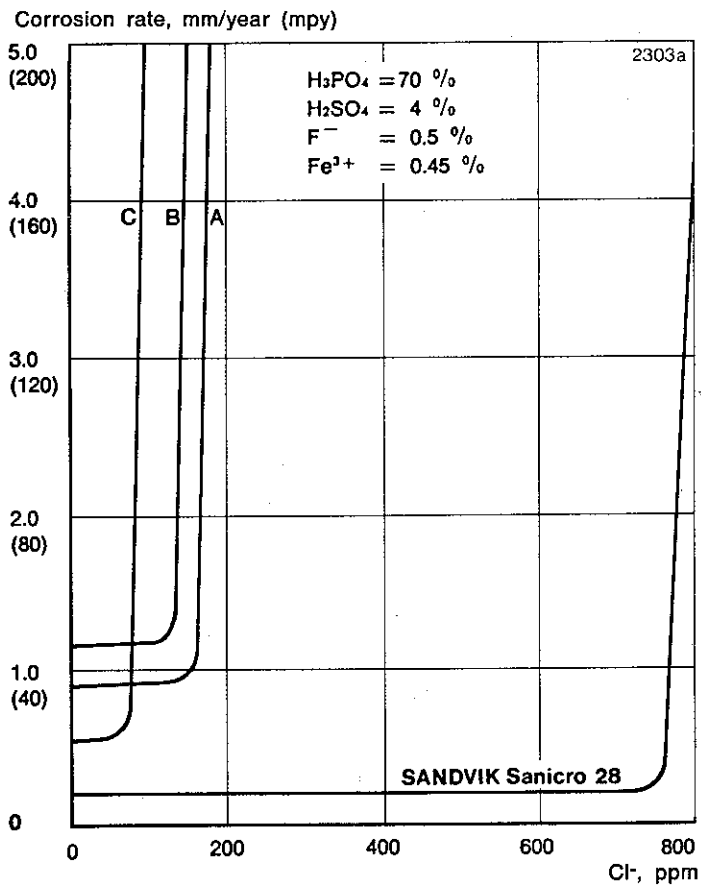


Figure 6 Influence of Cl^- content on the corrosion rates at 100°C of Sanicro 28 and alloys A, B and C (Table 2).

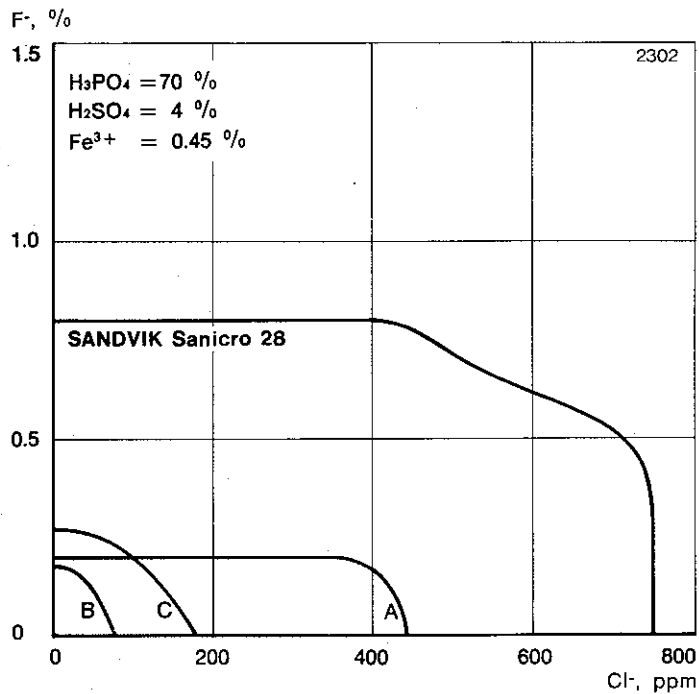


Figure 7 Combined effect of Cl^- content and free F^- content on the corrosion resistance at 100°C of Sanicro 28 and the alloys A, B and C (Table 2). In the areas under the curves, the corrosion rate is 0.3 mm/year or less.

Table 3. Effect of Al^{3+} and Si^{4+} on corrosion rates in 70% H_3PO_4 , 4% H_2SO_4 , 60 ppm Cl^- and 0.6% Fe^{3+} at 100°C

Grade	Total F^- content % by weight	Corrosion rate, mm/year		
		Al^{3+} content 0.4%	Al^{3+} content 0.8%	Si^{4+} content 0.4%
Sanicro 28	0.5	0.13	0.08	
	1.5	0.36	0.29	
	2.1	-	-	0.39
Alloy A	0.5	0.45	0.27	
	1.5	6.0	5.4	
	2.1	-	-	6.3
Alloy B	0.5	6.4	6.1	
	1.5	5.8	6.7	
	2.1	-	-	6.2

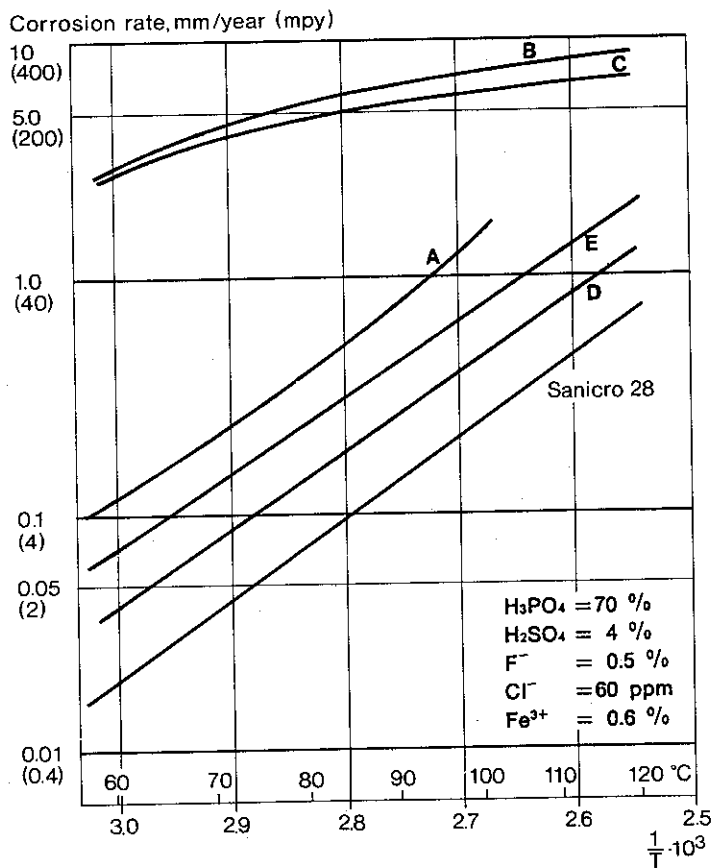


Figure 8 Effect of temperature on the corrosion rates of Sanicro 28 and alloys A, B, C, D and E (Table 2).

Table 2. Summary of the effect of the impurities in acid and of the alloying elements in steel on corrosion resistance in 70% H₃PO₄.

Impurities in acid	Alloying elements in steel	Effect on corrosion rate in the passive state	Effect on active-passive transition	Forms complex with F ⁻	Contributes to cathodic process	Net effect
F ⁻		Steep rise	Negative			Negative
Cl ⁻		No effect	Negative			Negative
H ₂ SO ₄		Indirect positive or negative effect through the effect on complex formation of AlF ₆ , SiF ₆	Negative			Negative
Si ⁴⁺		Reduction due to complex binding of F ⁻	Positive, due to complex binding of F ⁻	Yes		Positive
Al ³⁺		"-	"-	Yes		Positive
Fe ³⁺		No effect	Positive, by increasing the cathodic process	No	Yes	Positive
	Cr	Heavy reduction	Positive			Positive
	Mo	No effect	Positive			Positive
	Cu	No effect	Slightly positive			Slightly positive
	Ni	No effect	No effect			No effect

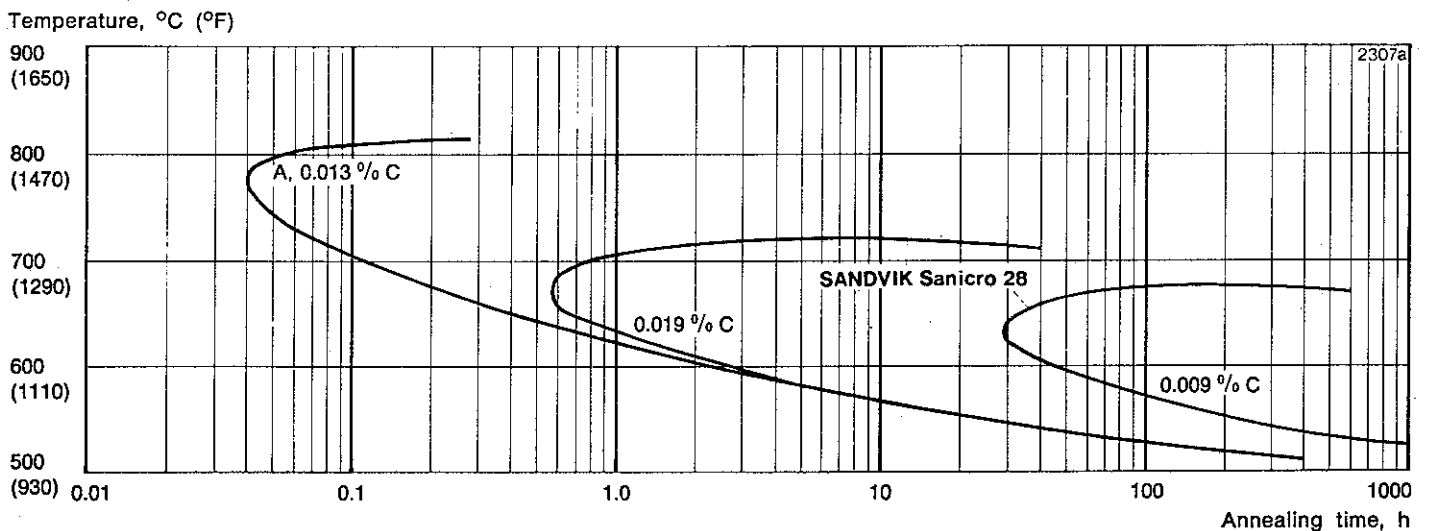


Figure 9 TTC diagram for SANDVIK Sanicro 28 with various carbon contents and steel A (analysis given in Table 2).

TEST EXCHANGER - SANICRO 28

Our paper noted that the primary intended application for Sanicro 28 is in heat exchangers used for the concentration of phosphoric acid.

As with most new alloys, laboratory data will generate interest, but acceptance normally requires that it be proven by exposure to, or use in the particular service for which it is intended.

To demonstrate the properties of Sanicro 28 and its viability as a suitable alternative to graphite, it was decided to have a small test exchanger built which could be operated in parallel with an existing evaporator tubed with graphite.

The exchanger for which we contracted (hereafter referred to as the "test unit") can be described as follows:

Forced Circulation Heat Exchanger
Shell - 10" diameter schedule 40 steel pipe
Tube Sheets - 1-1/2" thick, 20 Cr, 25 Ni, 4.5 Mo. 1.5 Cu
(drilled for 11 tubes)
Tubes - Sanicro 28, 1-1/2" O.D. x .059" MW x 16'0"
(secured with "O" rings)
Liquor Chambers - Two 10" diameter rubber lined tees

Operation and monitoring of Test Unit

In order to obtain data which would be beneficial to both operators and designers, the items below were to be monitored during each shift of operation.

- Steam Flow
- Steam Pressure
- Acid Temperature (in and out)
- Acid Concentration
- Specific Gravity of Acid

Supplementing this data are:

- Daily PH check of condensate
- Weekly acid analysis
- Monthly visual inspection of tubes
- Metalurgical examination of selected tubes after three months operation

The test is intended to be divided into two three month periods. In the initial period, the test unit has been operated in direct concert with the primary unit, including boil outs with a 5% sulphuric acid solution.

The second period will vary, in that the test unit, (to determine scaling characteristics) will not be subjected to the same frequency of cleaning as the primary unit.

This period is also needed to determine an annualized corrosion rate.

Installation

The test unit is operating in a northern Florida plant. A schematic of the installation is attached. The test unit was installed in parallel with a Karbate heater on an evaporator which is designated for 40% evaporation service. When filling the evaporator, such as after a boilout, the test unit is in contact with 28% acid. Thus, the test unit is in contact with acid in range of 28-40%. A seven day period between boilouts is typical.

Data Obtained

In the first six weeks of operation (1008 hours), the unit was in service 826 hours. The balance of the evaporator was either idle or down for maintenance or boilout. Five boilouts occurred during the period. After the first boilout, the tubes in the test unit were visually inspected and found to be clean with no scale build-up. This is noteworthy in that the test unit (inadvertantly) was not subjected to boilout, but merely drained.

During this six weeks, exit product temperatures ranged from 160 - 170°F with a maximum reading of 174°F.

An analysis of grab samples of evaporator liquor in contact with the test unit is below.

<u>P₂O₅%</u>	<u>F%</u>	<u>Solids%</u>	<u>SO₄%</u>	<u>Fe₂O₃%</u>	<u>Al₂O₃%</u>	<u>CaO%</u>	<u>MgO%</u>	<u>SiO₂%</u>	<u>Specific Gravity</u>
39.72	1.05	1.64	2.45	0.31	1.28	0.59	0.47	1.99	1.526
43.40	2.15	4.44	2.70	1.10	1.49	0.72	0.60	0.81	-
<u>46.95</u>	<u>1.94</u>	<u>5.03</u>	<u>5.43</u>	<u>1.32</u>	<u>1.69</u>	-	<u>0.78</u>	<u>0.38</u>	<u>1.674</u>
43.36	1.71	3.70	3.53	0.91	1.49	0.66	0.62	1.06	1.600 (Avg.)

In the second six weeks, the test unit was in service for 683 hours (vs. 1008 hours available). Six boilouts occurred during this time. Grab sample analysis for this period are below:

<u>P₂O₅%</u>	<u>F%</u>	<u>Solids%</u>	<u>SO₄%</u>	<u>Fe₂O₃%</u>	<u>Al₂O₃%</u>	<u>CaO%</u>	<u>MgO%</u>	<u>SiO₂%</u>	<u>Specific Gravity</u>
38.10	2.49	1.85	3.60	0.98	1.09	-	0.65	-	1.486
37.39	2.73	2.13	3.85	0.89	1.24	0.48	0.51	1.15	1.488
<u>42.03</u>	<u>2.55</u>	<u>3.05</u>	<u>1.80</u>	<u>1.11</u>	<u>1.39</u>	<u>0.59</u>	<u>0.59</u>	<u>0.24</u>	-
39.17	2.59	2.34	3.08	0.99	1.24	0.54	0.58	0.70	1.487 (Avg.)

The composite average for chlorides from all samples taken over the twelve weeks of operation is slightly higher than 100 ppm.

After a period of 120 days in service (including on-line, idle and boilout time) a single tube was removed from the test unit for metalurgical examination.

The tube was examined by the following means -

- Visually (with and without binocular)
- Light microscopy
- Scanning electron microscopy with edax

Results

- Visual Examination

The tube was found to be in good condition. A few minor longitudinal and/or spot-like surface markings were detected. These were identified as normal surface markings for seamless tubes. The wall thickness was measured and found to be within the tolerances for the as-produced tube.

- Light Microscopy

Some of the longitudinal and spotlike markings were investigated. The maximum depth found was 20 microns. This depth shall be compared with the defect depth allowed in ultrasonic testing of seamless tubing (80 - 160 microns, or 5 - 10% of wall thickness). If some of these markings are in fact related to corrosion, it would mean a corrosion rate of 0.05 mm/year above that of the overall general corrosion rate.

- Scanning Electron Microscopy

Tube samples were investigated up to 1000X magnification. The normal surface roughness of seamless tube materials was disclosed. In one case, an area with a slightly developed intergranular attack was studied. The maximum attack depth was estimated to less than 20 microns. The thin deposit on the I.D. of the tube was analyzed. Calcium, sulphur and phosphorus were the main constituents, and found in a ratio of 4/3/1. Some deposits contained potassium in amounts of 0.5 - 0.6 percent of the calcium content. These deposits also contained traces of aluminum and silicon.

Conclusion

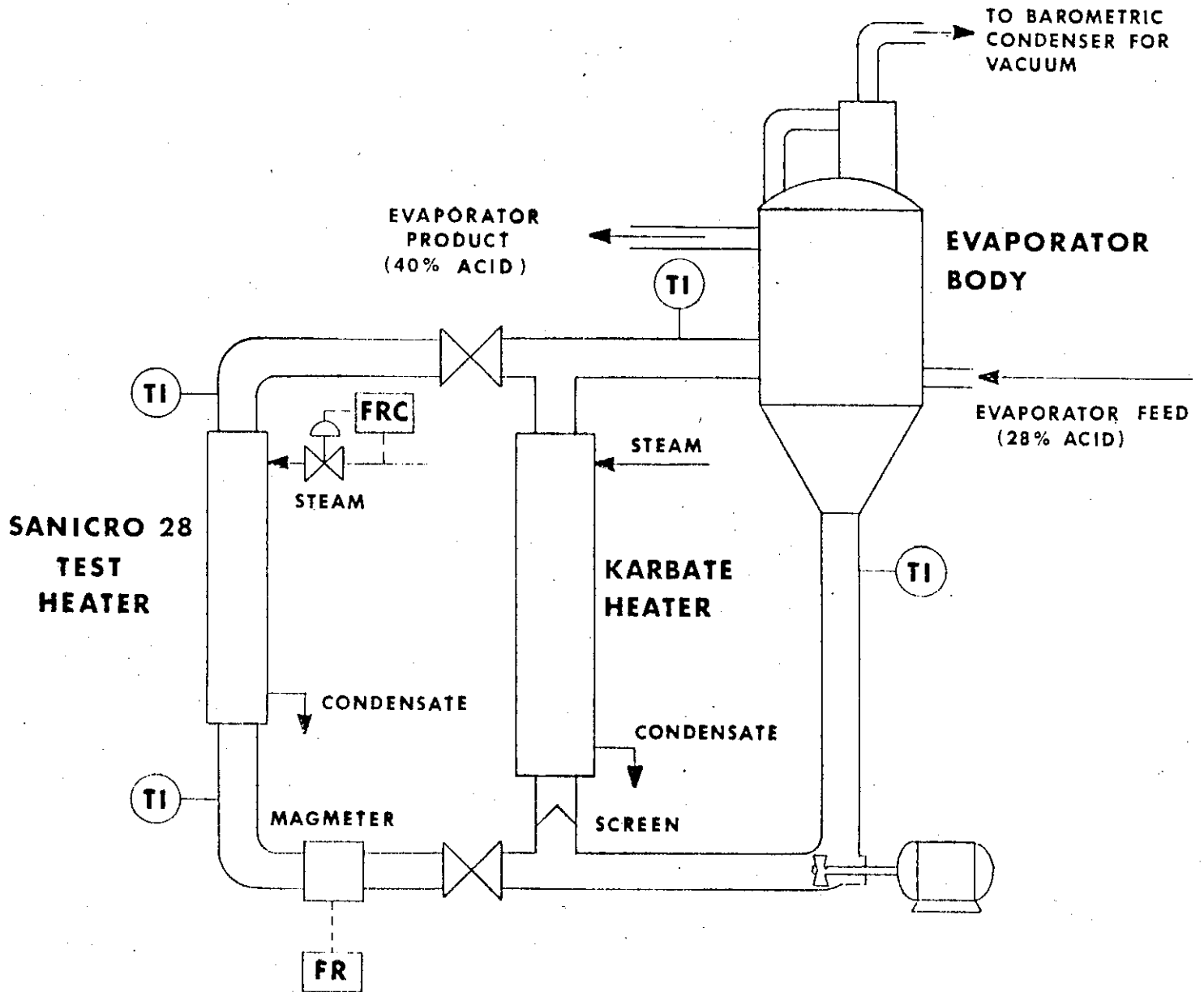
While it will take 10 - 12 months of service to establish a quantitative figure for the corrosion rate, it can be estimated at this time, that a rate in the range of zero to 0.2 mm/year can be expected.

Problems with the temperature measuring instruments during this period of operation preclude our reporting on heat transfer and fouling characteristics at this time.

This information and additional corrosion data will be compiled at three/four month intervals, and will be made available to all interested parties.

In conclusion, we can add that Sanicro 28 has been assigned UNS number N08028; is approved for Section VIII, Division I construction under ASME Code Case 1846; has an ASTM specification pending.

SANICRO 28 TEST HEATER INSTALLATION



NOTES

