PHOSPHORIC ACID EVAPORATION PROCESS IMPROVEMENTS LENGTHEN OPERATING CYCLE AND INCREASE PRODUCTION WITH CUSTOM-DESIGNED ALLOY

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A triple-effect evaporation system in a 650-s.ton/d phosphoric acid plant in Florida has been modified recently to operate in single-stage configuration. The principal objectives of this project were to increase capacity and to increase the length of production cycles, thereby increasing the total amount of finished product. However, an assessment of the revised process conditions confirmed that higher temperatures and thus more corrosive conditions would exist in the circulation systems. A detailed investigation was required in order to make the proper selection of alloy materials to be employed in the circulating pumps.

Many years of experience in processing various grades of phosphate rock at its Florida operation and a careful study of the experience of other producers in various parts of the world prompted the Royster Co. to evaluate a wide range of premium alloys as candidate materials for the evaporator circulating pumps. In order to meet their objective of longer operating cycles, it appeared necessary to upgrade alloy materials in these pumps, not only to compensate for the increase in corrosion severity but also to provide for a longer, more-reliable pumping operation than had been possible under the less severe original conditions using conventional alloy materials.

After a thorough evaluation of their operating history and the application of classic metallurgical judgements, Royster elected to specify a premium alloy custom-designed for their new pumping conditions. Modifications to a family of proven nickel-chrome alloys ultimately provided a custom material which was specifically engineered to the service and which, at the same time, could be produced reliably, consistently and economically.

The primary objectives of increasing production capacity and lengthening operating cycles are being fully realized. Such increased production has been achieved at modest capital cost and has resulted in significantly improved plant economics.

OPERATIONS DESCRIPTION

The Royster Co., located in Mulberry, Florida, is a producer of phosphate fertilizer products and currently manufactures approximately 320,000 s.tons/a of di-ammonium phosphate, 40,000 s. tons per year of triple superphosphate and small amounts of clarified phosphoric acid. The existing phosphoric acid plant was originally constructed in 1967, utilizing the Prayon process, with a rated capacity of 325 s.tons/d of P_2O_5. As a result of modifications beginning in 1967 and continuing through the revisions described in this paper, the operating capacity of this facility has been increased from the original 325 s.tons/d to a current capacity of 600 s.tons/d.

The supply of sulphuric acid for digestion is provided by a single-train sulphur-burning plant of Monsanto design originally built in 1967 with a rated capacity of 900 s.tons/d. Since that time, the plant has been modified to the double-absorption principle. As a result of a number of improvements and modifications, capacity has been increased to the present rate of 1,475 s.tons/d of sulphuric acid.

By 1981, it had become apparent that the evaporation section for concentration of filter acid represented a limiting factor in the production of phosphoric acid. This paper discusses modifications to the evaporation unit undertaken in order to increase rated capacity and total product throughput by means of lengthened operating cycles. As originally designed, the phosphoric acid leaving the filter section was concentrated from 29% to 54% P_2O_5 by triple-effect vacuum evaporation. While the use of the triple-effect arrangement does provide a modest theoretical advantage in terms of lower steam consumption,[1] it was Royster's belief that operating the evaporators as single-stage units in parallel would provide multiple benefits in terms of longer operating cycles, greater reliability and simplified operating control.[2,3,4]

Accordingly, a careful analysis of all factors relating to operation of the evaporation process was undertaken. In an evaporator unit, filtered acid of 29% concentration is heated indirectly by steam in a graphite shell-and-tube heat exchanger and delivered to a flash chamber. The system is maintained under vacuum by means of a barometric condenser. (See Fig. 1). In the flash chamber, water and volatile gas such as SiF_4 are evaporated. Circulation is maintained by the use of an axial-flow propeller pump designed to produce a high flow rate against a rather modest system head. These pumps are subjected to an extremely harsh environment and are often the source of considerable downtime and maintenance expense.

In addition to phosphoric acid, the circulating stream contains a quantity of surplus H_2SO_4 and abrasive gypsum solids, which add to its corrosive and erosive nature. Free fluorides and chlorides, the level of which can vary widely, depending upon the characteristics of the phosphate ores that are employed, also constitute very difficult contamination factors from the point of view of corrosion.

In Florida phosphate rock there is relatively little chloride, but a substantial amount of fluoride is present. A major part of the fluoride content is effectively not corrosive because it is tied up in the form of complex fluosilicates, and the presence of silica is, indeed, of benefit to the control of fluoride corrosion. Silica facilitates the formation of fluosilicates and the removal of fluorides in the form of SiF_4.[5] However, in processing Florida rock, a significant amount of fluoride does appear in the evaporator circuit as 1-2% HF. The combination of phosphoric, sulphuric and hydrofluoric acids at high temperature and velocity, together with abrasive solids, represents in total a truly formidable materials challenge.

ALLOY EVALUATION

In planning conversion of the three-stage triple-effect evaporator to single-stage parallel operation, Royster recognized that pumping duties would become more severe than originally encountered, inasmuch as all three circulating pumps would be operating in acid at the highest system concentration and temperature, in this case 52-54% P_2O_5 at 195°F (90°C). A study of their operating history with circulating pumps also revealed that the life of pumps made of materials such as Alloy 20 and CD4MCU left much to be desired, even when operating under the less difficult conditions Previous experience of Royster management in connection with the design and construction of phosphoric acid plants in other parts of the world also provided extensive background in the selection and operation of alloy equipment.

Accordingly, an analysis was undertaken of a wide range of premium alloys to seek the most suitable material for use in new evaporator circulating pumps required to optimize conversion to single-stage operation. It was believed that any incremental cost for a material that would increase pump life and extend operating cycles would be repaid quickly in terms of increased production. Various candidate materials were evaluated based on the knowledge that high chromium content is essential in providing a tough, corrosion-resistant film and that a substantial molybdenum content greatly enhances the formation of such a protective film and provides additional resistance to pitting and general corrosion. The materials to be favoured, of course, were the nickel-based austenitic alloys, particularly those containing substantial chromium and molybdenum.

In examining the alloys available for use in propeller pumps, Royster considered a range of materials, giving particular attention to the combined total content of chromium and molybdenum and to the total percentage of non-ferrous materials. Alloys considered or evaluated included a number of those in Table I, where they are listed in descending order of their chromium plus molybdenum content. Owing to variations which appear in published data representing complete chemical compositions of proprietary alloys, this paper will not attempt to include complete alloy analysis. Further information should be available from suppliers of candidate materials as listed in Table II.

As a result of the analysis and comparison of these alloys, modification of an existing premium alloy was undertaken to provide a higher combination of chromium molybdenum than any other material then available. The alloy selected and developed is known as Lewmet 25 (Table III).

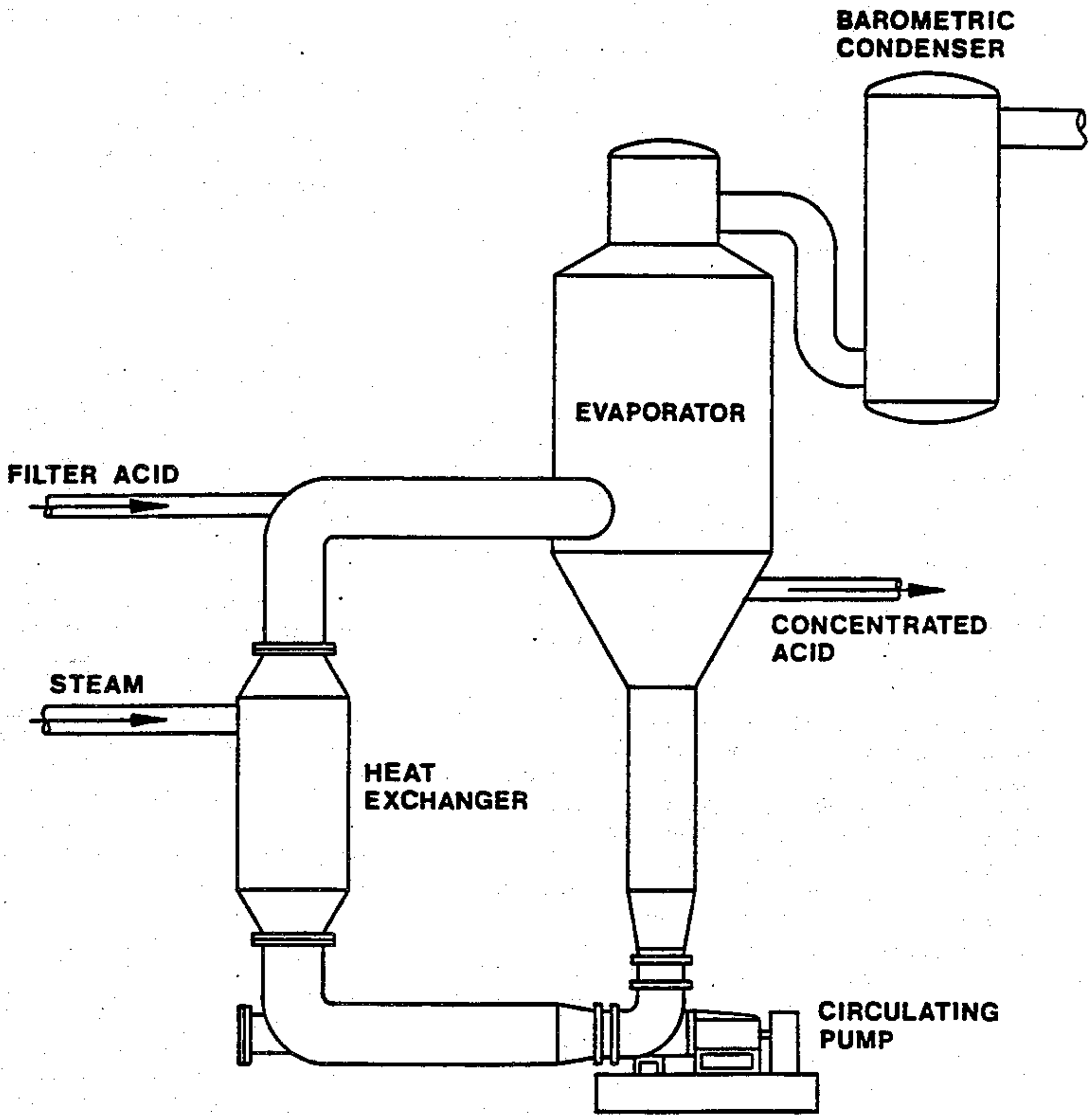

Fig. 1: Forced-Circulation Evaporator

Table I

Evaluation of Alloy Materials Commonly Used in Phosphoric Acid Service (nominal percentages)

Alloy[1]	Chromium	Molybdenum	Chromium + molybdenum total	Matrix structure[2]
Lewmet 25	29	4.5	33.5	A
Lewmet 15	28.5	2.25	30.75	Duplex-A & F
Sanicro 28	27	3.5	30.5	A
CD4MCu	26	2	28	Duplex-A & F
Ferralium	25	2.5	27.5	Duplex-A & F
Hastelloy G	22	6.5	28.5	A
Incoloy 825	21.5	3	24.5	A
Jessop 700	21	4.5	25.5	A
Carpenter 20 Cb-3	20	2.5	22.5	A
Alloy 20	20	2.5	22.5	Austenitic

1) Trademark ownership of these materials is shown in Table II.
2) A = austenitic, F = ferritic

Table II

Manufacturers of Corrosion-Resistant Alloys

Alloy trademark	Manufacturer
Alloy 20	(Non-proprietary)
Carpenter 20 Cb-3	Carpenter Technology Corp.
CD4MCu	(Non-proprietary)
Ferralium	Bonar Langley Alloys Ltd.
Hastelloy G	Cabot Corp.
Incoloy 825	The International Nickel Co.
Jessop 700	Jessop Steel Co.
Lewmet 15	Chas. S. Lewis & Co., Inc.
Lewmet 25	Chas. S. Lewis & Co., Inc.
Sanicro 28	Sandvik AB

Note: Some of the materials listed above may be available only in a cast form and others may be available only in a wrought form. Manufacturers may also have available an additional selection of alloys for specific duties.

Table III

Lewmet 25(R)

Nominal chemical composition

Element	Wt-%
Carbon	0.05
Silicon	0.50
Manganese	3
Chromium	29
Nickel	38
Molybdenum	4.5
Copper	3
Cobalt	6
Iron	15
Mechanical properties	
Yield strength, lb/in^2	38,000
Tensile strength, lb/in^2	70,000
Elongation, %	55
Reduction in area, %	60
Brinell hardness	146

(R) Registered trademark of Chas. S. Lewis & Co. Patents issued in the USA and other countries.

ALLOY DEVELOPMENT

In seeking an improved premium alloy for severe phosphoric acid service, the Lewmet^R alloy family, already widely employed in the fertilizer acid industry, provided the foundation. Lewmet 55, which is a nickel-cobalt-manganese base material, has been heavily utilized for the past 10 years for high-velocity wear components used in Chas. S. Lewis & Co. sulphuric acid tower circulating pumps and valves.[6,7,8] This material, which can be precipitation-hardened to levels of 500 Brinell, makes use of a complex austenitic matrix and contains a hard phase, rich in molybdenum and silicon. The hard phase is extremely beneficial in abrasive and strongly oxidizing acid streams. Lewmet 55 has also been successfully used in evaporator circulating pump service since 1977. Another Lewmet alloy (Lewmet 15) employs a high chromium-molybdenum content of 30.75% in an austenitic-ferritic duplex base. At the time of writing, evaporator circulating pumps of Lewmet 15 have been operating continuously for three years, with no corrosion attack, in another phosphoric acid plant located in nearby Nichols, Florida. These units are Lewis Type LH Size 24 (600 mm) propeller pumps rated at 17,000 US gal/min (3,864 m^3/h) handling P_2O_5 at conventional evaporator duty conditions. (See Fig. 2).

In developing a premium material for the Royster application, modifications to Lewmet 55 were undertaken to ensure resistance to fluoride attack by means of producing a totally austenitic single-phase alloy having enhanced levels of chromium and molybdenum and minimal silicon content. Lewmet 55 employs a complex elemental combination, rather than simply nickel, for its matrix. This matrix, which is a face-centered cubic structure, is found to have a capacity for accepting into an alloy solution a very high total content of body-centered cubic elements, such as chromium and molybdenum. Calculations of total alloy content within the matrix were made, taking into consideration the atomic size and weights of the elements. For a final determination of the maximum matrix capacity for chromium plus molybdenum, a series of experimental heats were designed, poured and then subjected to chemical, physical, and microscopic analysis. Scanning electron microscope analysis of the matrix, and of any second-phase precipitation, provided a precise chemical analysis of each formulation. In order to maximize the total chromium-molybdenum content, a composition was chosen at which the matrix is fully saturated in the as-cast form. After casting, a careful solution heat treatment is then employed to ensure a fully austenitic condition without the presence of a second phase.

Control of the silicon content, restricted to a level of 0.5 to 0.75%, is beneficial in increasing the chromium-molybdenum content and is also necessary to provide maximum resistance to HF corrosion under high-temperature conditions.

At this point, one might ask why the silicon should not be fully eliminated. Actually, it is not commercially practical to reduce silicon to a level below 0.5% since silicon is necessary to promote fluidity of the molten metal and regulate its oxygen content. Without some silicon content, pouring of the molten metal into a complex shape would be a practical impossibility. In addition, the component ingredients as used by the foundry are not available in a form totally free of silicon, except at a prohibitive cost.

The use of a substantial amount of cobalt appears to be unique to the Lewmet alloy family. Cobalt plays an important role in expanding the matrix structure and increasing the solubility of chromium and molybdenum. In addition, cobalt increases the level of hardness - or, more correctly, the alloy toughness - through a process of work hardening of the metal surface under the impact of abrasive solids.

In approaching the formulation of an alloy for the conditions encountered at Royster, the following requirements were defined:

Corrosion resistance - the alloy must be resistant to phosphoric acid and the impurities generally associated with wet-process acids; primarily, compounds of fluorine and chlorine and residual sulphuric acid.

Abrasion resistance - The alloy must resist the abrasive attack of gypsum particles not removed in the filtering process.

Castability - The alloy must be castable in commercial foundry practice and capable of yielding castings of the highest mechanical integrity.

Weldability - The alloy must be readily weldable utilizing conventional arc or inert gas procedures.

Lewmet 25 has been found to meet all of these goals. However, a design concept is only as good as the controls employed in the manufacturing process.

Observations of various failed alloy materials in phosphoric acid plants over many years have shown numerous cases of cracking, pitting, and intergranular corrosion. Many of the failures observed have obviously been caused by the lack of proper heat treatment procedures. In producing Lewmet 25, a precisely controlled solution heating treatment is employed. To provide a very positive method of insuring that heat treatment has been correctly executed, stringent quality control procedures are required. In particular, critical areas of individual castings are polished, etched and photographed by use of portable microphotographic equipment. In conjunction with certified chemical analysis, the photomicrographic analysis provides the final proof that a fully austenitic alloy structure has been achieved.

MODIFICATIONS AND RESULTS

In 1982, Royster, completed modification of the evaporator units to operating in single-stage configuration. Four axial-flow propeller pumps, Type LH Size 20 (500 mm), in Lewmet 25 construction, were provided by Chas. S. Lewis & Co. (Fig. 2). Three units were installed and one serves as a spare. Duty conditions are 12,000 US gal/min (2,727 m^3/h) at a pumping head of 12 ft (3.7 m).

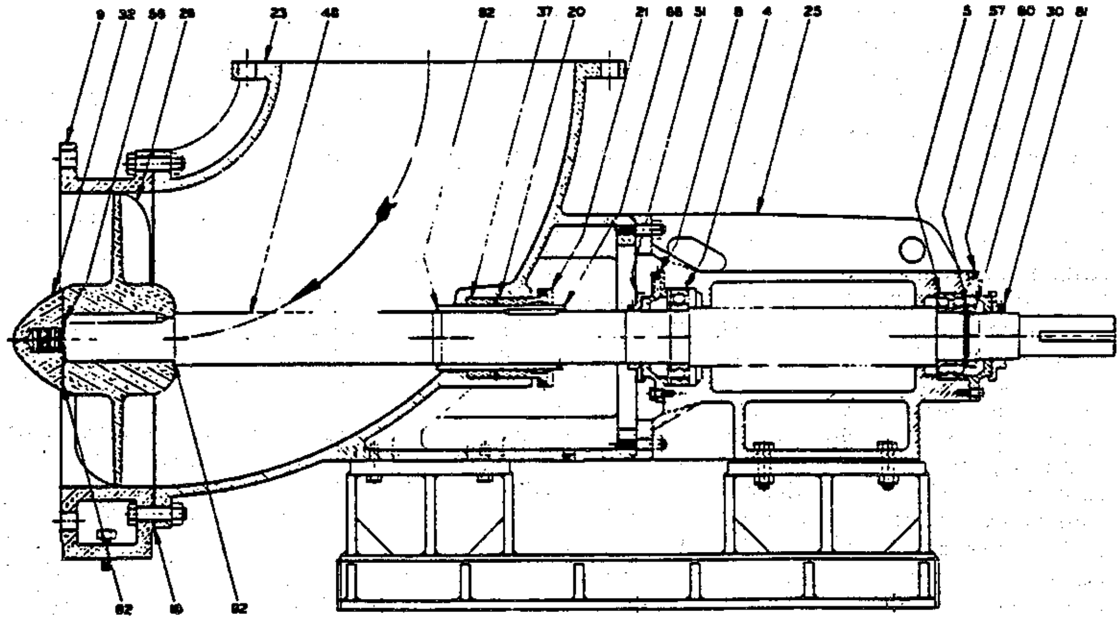

Fig. 2: Lewis Type LH Propeller Pump

Since the conversion to single-stage evaporation, each evaporator is operated continuously for a period of three weeks. One unit is removed from service each week for a planned wash/repair schedule. This washing process is performed by means of circulating approximately 10% sulphuric acid solution maintained at 180°F (82°C) for a period of 10-12 hours. Before conversion to single-stage alignment, the operating period for the first evaporator stage averaged 120 hours. The second and third stages averaged 175 hours. With the current single-stage alignment, the operation period for all units has been extended to 450 hours each. The phosphoric acid concentration operation no longer limits production of phosphoric acid despite operation at 185% of plant design.

In addition, the procedure required for placing a single-stage evaporator in service or for removing it from operation for routine wash/maintenance is greatly simplified, inasmuch as all three evaporator units are operating in parallel under the same process conditions. The shut-down or start-up of one unit has no effect on the performance of the remaining two units. This is in sharp contrast to the upset condition imposed on the two units remaining in operation when one unit of the three-stage alignment was removed from service either on a planned or emergency basis.

In carrying out the modification, circulation rates have been increased, resulting in higher velocities through the heat exchangers. Higher velocities have been beneficial in reducing scale formation and thus in lengthening the operating cycle as described above.

As another step in maximizing production, the amount of water to the circulation pump packing glands is carefully monitored and controlled. Royster has chosen a combination of Kevlar(R) and carbon ring packing in installed flow measurement devices to control water injection to the lantern glands. Monitoring of the stuffing box packing adjustments have been assigned exclusively to plant mechanics rather than evaporator operators. Water flow to the packing averages 0.5 US gal/min (1.9 litres/min) per pump and never exceeds 1.0 US gal/min (3.8 litres/min).

Expected benefits from the evaporator modification programme have now been fully demonstrated through one full year of operation. The plant operating factor, exclusive of an annual turnaround of 2-3 weeks, has increased from 72-74% to a present level of 88-90%, with an associated phosphoric acid annual production increase to approximately 195,000 s.tons of P_2O_5. This increase in production has been achieved with modest capital investment and should be a significant factor in extending the profitable operation of the Royster facility for many years to come. The use of premium alloy circulating pumps has been a significant contribution to the project's success.

REFERENCES

1. Martinez, J. L.: "Energy savings in a new phosphoric acid plant". AIChE National Meeting, New Orleans (Nov 1981).
2. Martinez, J. L., and Snell, H. A.: "Single-stage evaporation of wet process phosphoric acid". AIChE Joint Meeting, Daytona, FL (Nov 1974).
3. Martinez, J. L., and Miller, D.: "Single-stage evaporation of wet process phosphoric acid". AIChE Florida Section Meeting, Lakeland, Florida (Nov 1974).
4. Martinez, J. L.: "Advances in phosphoric acid evaporation and clarification". American Chemical Society, 185th National Meeting, Kansas City (Sept 1982).
5. Rushton, W. E.: "Defluorination of wet-process acid", Chemical Engineering Progress (Nov 1978), 52.
6. Clayton, C. H., and Johnson, T. E.: "Engineering materials for pumps and valves", Chemical Engineering Progress (Sept 1978), 54.
7. McClain, G. E.: "Materials and technology considerations in sulphuric acid energy recovery". In "Making the Most of Sulphuric Acid": Proceedings of the British Sulphur Corporation's Fifth International Conference, London (Nov 1981).
8. McClain, G. E., and Mueller, W. A.: "Corrosion problems in acid flow control". Chemical Engineering Progress (Feb 1982), 48.
9. Houghtaling, S. V., and Rushton, W. E.: "Sludge recirculation process for phosphoric acid concentration". AIChE Symposium on Processing Phosphate for Fertilizers (Feb 1968).

(R) Registered trademark of E. I. Du Pont de Nemours & Co., Inc.