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## ALTERNATE MATERIALS OF CONSTRUCTION FOR THE LANTHANUM FLUORIDE PROCESS

### INTRODUCTION:

The $BiPO_4$ Separations Plant equipment and process piping were fabricated of 309 SCb stainless steel based on original corrosion data. Subsequent corrosion data have shown that this was a good choice. The rather extreme conditions encountered in the lanthanum fluoride cycles, however, have resulted in frequent failure of the HF addition dip tubes and less frequent but increasingly prevalent failure of the HF solution process lines. Audigage measurements of the process vessel wall thickness have indicated very little corrosion of the tanks. Reported difficulties in the procurement of 309 SCb stainless steel make it advisable that an alternate material be designated for use in the lanthanum fluoride precipitation steps.

### SUMMARY:

Based on information received from the Purchasing Unit, Type 309 SCb stainless steel is apparently no more difficult to procure than is Type 304L or 347 stainless steel. Because of currently low stocks either type requires three to six months to procure. Because of the relatively small quantities (about 1,000 ft.) of pipe required in the lanthanum fluoride step (tanks are excepted because it is reported that spares are available), it would appear that judicious procurement of Type 309 SCb stainless steel



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now for delivery three to six months hence should insure trouble-free operation for another seven to ten years. However, since other unknown factors may enter into the request for alternate materials of construction it is assumed that Type 309 SCb stainless steel is impossible to procure.

Corrosion studies recently carried out by the Corrosion Studies Group, in which Type 309 SCb, 304 L, 347, and 321 stainless steels were exposed to simulated lanthanum fluoride by-product and product solutions indicate that Type 304 L stainless steel corrodes at about twice the rate of Type 309 SCb (0.002 in./mo. vs. 0.001 in./mo.). Since the existing process piping has lasted about seven years, it is reasonable to expect that replacement pipe of Type 304 L would last from three to five years. Consequently Type 304 L stainless steel is recommended as an alternate material of construction with the understanding that corrosion rates will be higher but not excessive. Type 308 L welding rod should be used when welding Type 304L stainless steel. Heat treatment is not required. As a confirming test, it is suggested that a section of existing pipe in the process be replaced with Type 304L pipe to evaluate the material under actual process conditions.

The HF addition dip tubes present a special problem since failure of these tubes has been high. It is recommended that a dip tube with a Teflon tip be fabricated and installed in the process to determine if greater life expectancy can be obtained. A suggested method of fabricating a dip tube with a Teflon tip is described.

DISCUSSION:

The lanthanum fluoride cycles are performed in three cells in the concentration (224) Buildings, i.e., by-product precipitation in D Cell and product precipitation in B and E Cell (parallel operation). During processing, anhydrous HF is added to the process solutions to give final compositions as follows:

By-Product Precipitation

| | Per Cent | Molar |
|---|---|---|
| $HNO_3$ | 8.5 | 1.41 |
| $H_3PO_4$ | 0.8 | 0.08 |
| $Na_2Cr_2O_7$ | 0.1 | 0.005 |
| $KMnO_4$ | 0.1 | 0.009 |
| HF | 0.4 | 0.19 |
| $LaF_3$ | 0.2 | 2,140 mg./l. |
| $H_2SO_4$ | 0.06 | 0.006 |
| $(NH_4)_2SO_4$ | 0.06 | 0.005 |
| $KNO_3$ | 0.04 | 0.004 |

Prior to the HF addition, oxidation with the $KMnO_4$ is performed at 75°C. A maximum temperature of 35°C. is maintained during and after the HF addition.

Product Precipitation

| | Per Cent | Molar |
|---|---|---|
| $HNO_3$ | 7.1 | 1.17 |
| $L_3PO_4$ | 0.5 | 0.05 |
| $NaNO_3$ | 0.03 | 0.003 |
| $KNO_3$ | 0.1 | 0.01 |
| HF | 1.0 | 0.52 |
| $LaF_3$ | 0.03 | 252 mg./l. |
| $Mn(NO_3)_2$ | 0.2 | 0.01 |
| $H_2C_3O_4$ | 0.3 | 0.030 |
| $Cr(NO_3)_2$ | 0.2 | 0.006 |
| $NH_4NO_3$ | 0.02 | 0.003 |
| $H_2SO_4$ | 0.04 | 0.004 |
| $(NH_4)_2SO_4$ | 0.04 | 0.003 |

Max. Temperature 35° C.

In service, the anhydrous HF addition tubes fail after 150 to 250 runs are processed. Failure of the dip tube is by dissolution of the end of the tubes. These are constructed of 1 and 2-inch pipe approximately 8 feet long. Process piping failures have occurred at irregular intervals and became frequent after approximately seven years of service. Failure in general has been in the pipe proper. Field repair by welding has been unsatisfactory with failures of the repair weld occurring within two to six weeks. Approximately 1,000 feet* of 2-inch pipe are exposed to the HF solution. Process tanks have not shown evidence of corrosion failure. Audigage measurements of the tank (ca. 1950-1951) indicated no decrease in the thickness of the walls. Spare tanks are available for replacement if necessary.

Recent corrosion tests of 304L, 347, and 321 stainless steels in simulated lanthanum fluoride by-product and product solutions by the Corrosion Studies Group, reported in HW-28699 (not yet published) indicate that the 18-8 stainless steels are not quite as satisfactory as 309SCb (CN-1314, 1628, and 1872), and that maximum corrosion rates are experienced in the product precipitation step. A summary comparison of the corrosion rates in simulated product precipitation solution is as follows:

| | |
|---|---|
| 304 L | 0.002 in./mo. |
| 347 | 0.001 - 0.003 in./mo. |
| 321** | 0.001 in./mo. |
| 309 SCb | $\leq$ 0.001 (From CN reports) |

On the basis of these tests, the use of Type 304L welded with 308L as a substitute for 309SCb is recommended with the understanding that the corrosion resistance of 304L will probably not be equal to that of 309SCb.

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* Rough estimate from Manufacturing.

** Test with 321 not conclusive -- single heat tested.

The use of a plastic dip tube for HF addition has been considered but the 75°C. temperature imposes a severe restriction on the use of any plastics other than Teflon or Kel-F. Manufacturer's data are available on the following:

Teflon and Kel-F - Excellent in $HNO_3$ and in HF at process temperatures.

Polyethylene - Satisfactory in $HNO_3$ and in HF at 140°F. (60°C.). Softening point listed as 100 - 115°C.

Uscolite (acrylic) - Satisfactory in 10% $HNO_3$ and in HF below 170°F. (77°C.). Fair in (10% - 25%) $HNO_3$.

Saran - Excellent in 48% HF at 77°F. (25°C.). No data above. In 10% $HNO_3$, excellent at 77°F. (25°C.), good at 122°F. (50°C.) and poor at 167°F. (75°C.).

PVC - (Boltaron 6200) - Fair in 48% HF at 24°C. No data above. In 10% $HNO_3$ excellent at 24°C. and 52°C., fair at 60°C.

Data are not available for HF-$HNO_3$ mixtures.

Kel-F or Teflon will withstand the temperature conditions but are not readily available in pipe form. A suggested modification to the dip tube employing a Kel-F or Teflon tip, fabricated from tubing, is shown in the attached Figure. The proposal involves the use of a standard size Teflon tube section 7/8 in. i.d. by 1.5 in. o.d. which is attached to the 1 in. i.p.s. dip tube by the use of a special stainless steel threaded coupling. The 1 in. i.p.s. addition pipe would be cut just below the shroud, threaded, and the special coupling attached. The lower end of the coupling would be threaded with machine threads to match the specially threaded end of the plastic tubing. Approximately 6 in. of Teflon tubing would be required to provide the necessary length.

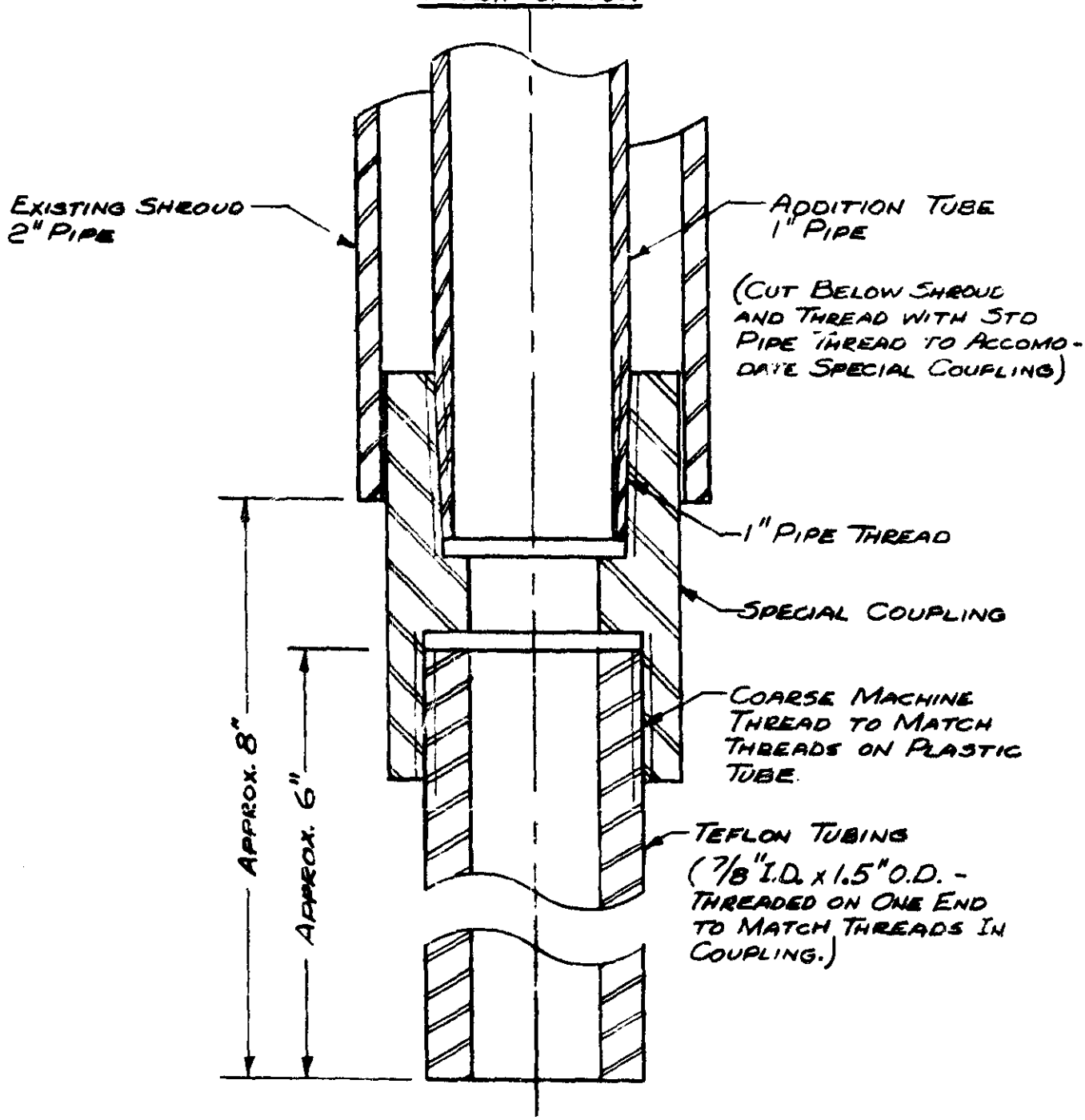
RECOMMENDED PROGRAM:

On the basis of existing corrosion data, no further laboratory work is suggested. It is recommended that a piece of process pipe in the plant be replaced with a section of Type 304L pipe welded with Type 308L welding rod. Heat treatment is not recommended. Observation of the performance of this pipe will provide a basis for specifying Type 304L pipe as a permanent replacement for Type 309SCb.

It is recommended that a dip tube containing a Teflon tip be fabricated as suggested in Figure 1. (Teflon is recommended because it is normally cheaper than Kel-F.

# FIGURE 1

## PROPOSED DIP TUBE MODIFICATION

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