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DESIGN AND APPLICATION OF CORROSION-RESISTANT HEATED TRANSFER TUBES FOR LIQUID METALS AND SALTS

by

D. E. Grosvenor, I. O. Winsch,
W. E. Miller, G. J. Bernstein,
and R. D. Pierce

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ABSTRACT

Pyrochemical processes under development at Argonne National Laboratory use liquid metals and molten halide salts as solvents to separate molten fuel materials from each other and from fission products. These solvents are moved between process vessels by pressure-transferring through resistance-heated transfer tubes operating at temperatures up to 850°C. The transfer tubes are J- or U-shaped and are fabricated from gun-drilled molybdenum-30 w/o tungsten bar stock. The tubes are shaped by hot-bending them in a jig. A technique for joining two pieces of tubing had to be developed because of the limited overall length of tubing available. The transfer tubes are wrapped with resistance heaters, covered with insulation, and protected by steel shells. Temperatures are controlled by adjusting the voltages in the various heater circuits.

INTRODUCTION

The Chemical Engineering Division at Argonne National Laboratory has developed several pyrochemical processes for the recovery and purification of fast-reactor fuels. Pyrochemical processes are high-temperature processes for separation of fissile fuel materials from fission-product contaminants. The pyrochemical processes that have been or are being developed include the melt-refining process,¹ the skull-reclamation process,^{2,3} and, most recently, salt-transport processes.⁴

The transfer of molten salts and metals from one vessel to another is an essential part of most pyrochemical processes. The transfer system must be reliable, simple, and compatible with remote operation. The transfer tube must be resistant to the salts and metals used in the process at temperatures up to 850°C. A number of transfer tubes were built for use in pilot-plant and full-scale operations. This report describes the methods of construction used in the development of transfer tubes and applications of the tubes in a variety of pyrochemical processes.

FABRICATION OF MOLYBDENUM-TUNGSTEN TUBES

Three criteria were used in selecting a material for construction of transfer tubes: (1) structural strength at operating temperatures up to 850°C, (2) resistance to corrosion by halide salts and metals, such as zinc and zinc-magnesium alloys at 800°C, and (3) fabricability of the material by available techniques. Corrosion resistance to zinc at 800°C narrowed the choice of materials to tungsten and molybdenum-tungsten alloys such as Mo-30 w/o W.⁵⁻⁷ Although the corrosion resistance of tungsten at high temperatures led to its use as a crucible material for containment of process solutions, the extreme difficulties normally encountered in machining and forming tungsten eliminated it from consideration for fabrication of transfer tubes.

Tubing made by drawing or extrusion is still in the research stage and is not available; therefore the tubing was made by gun-drilling swaged bar stock. The usual procedure was to drill from both ends toward the center. Four kinds of tubing were produced: 1/2-in. OD, which was drilled to a 1/4- or 5/16-in. ID, and 3/4-in. OD which was drilled to a 3/8- or 1/2-in. ID. Because of the limitation on the depth to which a rod can be drilled without excessive runout (usually about 200 times the diameter), the

maximum drilled lengths available on regular order were about 36 in. for the 1/2-in.-OD tubes and about 48 in. for the 3/4-in.-OD tubes. However, tubes 72 in. long have been made on special order.

308-1018

Fig. 1. Initial Design of Mo-30 w/o W Transfer Tube Using Threaded Elbows and Tubing

Since the total length of tubing required for a transfer tube is between 6 and 8 ft, suitable methods for joining the tubing were needed. The tubes could not be joined by welding because the area near the weld became embrittled. Originally, threaded connections were used to join the tubes. In general, only one threaded coupling was used in a transfer tube, although at one stage in the development of the U-shaped 1/2-in.-OD tube, two threaded elbows were used to form the tube (see Fig. 1). Threaded tubes of the required lengths were screwed into the elbows. This method of construction proved to be impractical because of (1) the difficulties encountered in machining the pipes and elbows to the precision required to hold the

three straight lengths of tubing in the same plane, (2) the long machining time required, and (3) the development of occasional leaks at the elbows. The Mo-30 w/o W alloy is difficult to machine because it is hard and brittle at room temperature. However, the alloy can be machined satisfactorily if the cutting tools are sharp and are ground to a positive rake of 25-27°, and if a cutting oil* is used to prevent the tools from overheating.

A method of bending the Mo-W tubing into a U shape was developed that eliminated the need for the troublesome machined elbows. This technique was used in fabricating the first plant-scale transfer tube. The transfer tube was made from two lengths of 3/4-in.-OD by 1/2-in.-ID tubing joined by a threaded coupling. The tube was hot-formed in a bending jig (shown in Fig. 2). The bends were made around a Mo-30 w/o W wheel that was attached to a 10- by 30-in. steel channel equipped with appropriate clamps to hold the tubing. The tubing was heated to approximately 1400°C with three oxyacetylene torches. To avoid excessive oxidation of the tube, the torch flames were adjusted to be slightly reducing, and the inside of the tube was purged with a stream of argon. A close-fitting pipe was then slipped over the free end of the tube for added leverage during the bending operation. Stop pins mounted in the steel channel determined the angle of the bend. Both bends were made in the same length of tubing, one end of which had been threaded to fit a Mo-30 w/o W coupling threaded on a second straight length of tubing.

108-9860

Fig. 2. Bending Jig for 3/4-in.-OD Mo-30 w/o W Transfer-tube Tubing

The construction of the threaded joints was critical to their successful performance. The form of thread used was a modified Whitworth thread with 16 threads to the inch. The fine threads and rounded roots were used to reduce the chance of breakage, since the Mo-W alloy is very notch-sensitive. The coupling was threaded from both ends, and the threads terminated in a flat-faced shoulder at the middle of the coupling. Since the

*Tap Magic, The Steco Corporation, Little Rock, Arkansas.

Mo-30 w/o W alloy is subject to seizing and galling, the threads were cut to a fairly loose fit to be certain that the tubes could be turned all the way into the coupling against the shoulder. A seal was made with a 0.010-in.-thick tantalum gasket placed between the butt end of the tube and the internal shoulder in the coupling.

The two sections of tubing were then sealed and locked to the coupling by back-brazing the joints with a palladium-nickel alloy.* The brazing operation was carried out in an argon-atmosphere glovebox to prevent oxidation of the parts. Before being placed in the glovebox, the parts were cleaned by sand-blasting with fine alumina grit. During the brazing operation, the joint was inductively heated to the melting point of the braze material, which was applied using Nicrobraz flux.** Transfer tubes joined in this way have proven to be leak-tight and reliable.

RESISTANCE HEATERS

The transfer tubes were heated by several resistance heaters wound closely around the tubes. Two different types of heaters were tested for this purpose. The first type of heater consisted of a Nichrome heater wire enclosed in a swaged 1/8-in.-OD Inconel jacket insulated with magnesia powder. This type of heater gave good service at temperatures up to 800°C (provided high-quality units were used) and was particularly suited to transfer tubes that required frequent handling or installation in test equipment. The heaters were resistant to mechanical shock and could be bent without damage. However, failure of any one heater required the complete rebuilding of the heater assembly and the outer support case. The failures that occurred were thought to be caused by traces of moisture in the magnesia insulation which, at 800°C, produced pressures sufficiently high to burst the Inconel sheath.

A transfer tube wound with swaged heaters is shown in Fig. 3. The heater ends are brought out through compression seals in one side of the jacket as shown. Two jacket halves are welded together and form a leak-tight enclosure.

The second type of resistance heater tested was a cable made of stranded Chromel heater wire insulated with refractory braid and wrapped by a stainless steel winding. The cable was designed at Argonne and produced by Claude S. Gordon and Company. Specifications for the cable (shown in Fig. 4) are given in Table I.

*Product of American Platinum and Silver Division of Engelhard Industries, Newark, New Jersey.

**Product of Wallcolmonoy Company, Detroit, Michigan.

108-8228

Fig. 3. Complete Transfer-tube Assembly Using Inconel Jacketed Heaters

108-9033

Fig. 4. Chromel Heater Wire Insulated with Refractory Braid and Wound with Stainless Steel

TABLE I. Specifications of Heating Cable

Wire type	Chromel P, No. 14 stranded
Cover	Spiral-wound stainless steel ribbon
Insulation	Double-layered vitreous silica braid
Nominal resistance	0.1 ohm/ft
Overall diameter	0.15 in.

This cable had three advantages over the swaged heaters: (1) It could be produced in unlimited length, (2) it was far more flexible, and (3) it was not subject to the moisture problems experienced with the sheathed heaters. The first two features made it possible for the cable to be wound

rapidly and easily as a double spiral with both ends terminating at the same place on the transfer tube.

The manner of winding the cable around a tube is shown in Fig. 5, which is a photograph of a wound test specimen used to evaluate the performance of a heater. The figure also shows how the cable was tied in place with Refrasil* insulating tape. The tape was then wrapped with stainless steel shim stock held in place by stainless steel wire.

108-9035

Fig. 5. Heating Cable Wound on Test Assembly

* A silica insulation product of Hitco (H. I. Thompson Fiberglass Company), Gardena, California.

INSULATION

Two types of insulation were used to cover the resistance heaters that were wrapped around the Mo-30 w/o W tubes. Areas that were open to direct access were wrapped with several layers of 1/4-in.-thick Fiberfrax* sheet. This insulation was tied in place with Refrasil tape. Tapes containing organic adhesives had to be avoided in applications in which the stranded resistance heaters were used. The organic materials volatilized when the tube was first heated, and the vapors penetrated the braided insulation, where they carburized and shorted out the heaters. Even inorganic electrical insulation such as Refrasil contained a trace of organic lubricant used in its manufacture that had to be volatilized by heating the finished transfer tube slowly in air before it was put into service, thereby oxidizing the organic material.

108-8170

Fig. 6. Transfer Tube for Use in Argon Atmosphere

The vertical sections of the transfer tube were enclosed in sealed stainless steel jackets and therefore could not be wrapped with Fiberfrax. These sections were packed with Tipersul.**

CORROSION PROTECTION

The large transfer tube shown in Fig. 6 was built for use in an argon atmosphere environment in the EBR-II Fuel Cycle Facility. Accordingly, it was not necessary to provide a leak-tight jacket to protect the Mo-30 w/o W tube and the heaters against oxidation at operating temperature. The outer jacket was simply clamped over the insulation to provide mechanical protection and support.

The first transfer tubes built were used in an air atmosphere, which caused serious and rapid oxidation of the Mo-30 w/o W tubing and occasionally resulted in the failure of a tube. To alleviate this problem,

subsequent transfer tubes were built with a gas-tight stainless steel case that covered the part of the tube normally exposed to air. The annular space between the tube and the case was purged continuously with an inert gas to prevent oxidation of the tube.

*An alumina-silica fibrous insulation manufactured by the Carborundum Company.

**Fibrous potassium titanate made by E. I. Du Pont de Nemours & Company.

Hot fumes from the molten-salt and liquid-metal solvents also created a corrosion problem. Although only the bare Mo-30 w/o W tube was submerged in the molten-salt and liquid-metal solvents, the hot fumes above the surface of the melt corroded the heaters and the stainless steel jacket around the insulation. Therefore, protection for the heaters and the jacket was provided by a Mo-30 w/o W protective cup sealed to the tube with a Mo-W ferrule as shown in Fig. 7. The cup was about 9-10 in. long, had an

308-1017

Fig. 7. Final Design of Transfer Tube for EBR-II Fuel Reprocessing

ID of about 2 in., and had internal threads at the lower end. The cup was machined using the techniques developed for machining the Mo-W tubing, but the machining was carried out at -40°C . Excellent tolerances (± 0.0005) and finish, not possible at normal temperatures, were achieved at -40°C .

TEMPERATURE CONTROL

The operating temperatures in a transfer tube were maintained slightly higher than the temperature of the molten salt or metal being transferred to avoid cold spots in the tube where the material might freeze, particularly at the start of flow. Once the molten material was flowing through a tube, a uniform temperature was established and the risk of plugging the tube was minimal.

Each heater circuit was independently controlled by its own variable transformer to regulate current and voltage. The power that had to be supplied to any section of the transfer tube depended directly upon the rate of heat loss at operating temperature. Thus, less power was required in the vertical section of the transfer tube that was located within the process furnace. Where the power requirement varied over a single heater circuit, the spacing of the heater coils was varied as required to increase or decrease the heat input in a specific zone. Since the heat loss at the discharge end of a transfer tube was higher than at an intermediate position, additional heat input was required at this point. Additional heat was provided by adding an extra layer of heater windings and attaching a pancake resistance heater to the outside of the tube at the discharge end.

Thermocouples were installed at critical positions along the heated section of the transfer tube to monitor tube temperatures. Temperature profiles were established by moving a thermocouple through the inside of a hot transfer tube. This test determined the uniformity of heating along the tube, and was a check for possible cold spots where the molten salts or metals could freeze at the beginning of a transfer. Experience had shown that the electric current required to hold a transfer tube at operating temperature remained nearly constant from run to run. In 24 transfers there was no indication of heater degradation as indicated by changes in resistance or leakage to ground. Table II lists typical power inputs to the heaters for a transfer tube used to make transfers at 800°C .

TABLE II. Power Requirements for Transfer at 800°C
with Plant-scale Transfer Tube Shown in Fig. 7

Heated Zone Location	Heated Zone Length, in.	Volts	Amps	Watts
Furnace downleg	34.5	37	7.0	260
Horizontal section	18.5	25	8.7	218
Discharge end	19	25	8.1	202
Pancake heater at discharge end		208	5.7	1200

APPLICATION TO PYROCHEMICAL PROCESSES

Resistance-heated Mo-30 w/o W transfer tubes have been used in all phases of development of the skull-reclamation process, blanket process, and salt-transport process.

In some early applications, the transfer tube was sealed to the process furnace with a water-cooled rubber compression seal. However, no organic or water-cooled seals were permitted in the plant-scale skull-reclamation furnace. Consequently, the transfer tube was sealed to the furnace with a fusible metal seal.⁸ The skull-reclamation furnace transfer line gave excellent service with the furnace. Figure 7 shows the transfer line installed in the top of the skull-reclamation furnace. Figure 8 is a photograph of the transfer tube mounted in the top of the furnace. The J-shaped transfer tube was used whenever molten material was to be transferred from a furnace to an open receiver. The large bellows at the discharge end of the transfer line was used to make a seal with a transfer receiver hood. This hood was used to prevent the escape of salt and metal fumes when molten salts and metals were transferred out of the furnace into open containers.

108-8244

Fig. 8. Transfer Tube Mounted in Top of Skull-reclamation Furnace Bell Jar

In the salt-transport process currently under development, molten salt is cycled back and forth between two furnaces containing liquid metal.

For this process, a U-shaped transfer tube is used in which both vertical legs are the same length. The ends of the vertical legs extend down to a point just above the molten salt-liquid metal interface. Salt is transferred in either direction by pressurizing the discharging furnace and venting the receiving furnace.

CONCLUSION

Methods of fabricating gun-drilled molybdenum-30 w/o tungsten alloy rod into various configurations for transfer tubes have been developed. The transfer tubes, which are resistance-heated, have been used with a high degree of success for transferring liquid metals and molten salts at 800°C with pressure-transfer techniques.

ACKNOWLEDGMENTS

We wish to thank T. F. Cannon, A. L. Chandler, R. C. Paul and G. Rogers of the Chemical Engineering Division and L. Kinkel, R. F. Malecha, and R. C. Stimac of the Central Shops for their valuable technical assistance in the development of the heated transfer tubes.

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