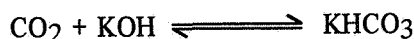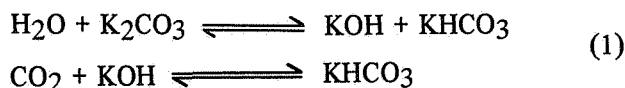# Packings for Hot Carbonate Systems

Carbon steel and polypropylene packings have been proven suitable for most hot carbonate systems. Ceramic packings have not given reliable service, and those made from stainless steel are simply too expensive for most plants.

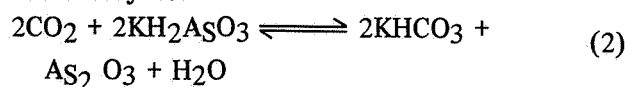P. A. Ruziska, Exxon Chemical Co., Florham Park, N.J.

During the past ten years, each type of tower packing material (with the exception of stainless steel) used in our hot carbonate CO_2 removal units has caused a number of major unit upsets. Many have resulted in plant shutdowns and some have resulted in the loss of the downstream methanation catalyst charge. As inferred in Table 1, economics strongly favor avoiding stainless steel packing. The additional cost of stainless steel can add $250,000 to $500,000 to the cost of a large ammonia plant. Obviously, we prefer to use the lower cost materials if at all possible. Note also that the price differential is small for ceramics, polypropylene, and carbon steel. This means we can concentrate on other aspects such as strength, thermal stability, and corrosion resistance in selecting which of these three materials to employ.

The basic chemistry of the commercial potassium carbonate system is shown below:
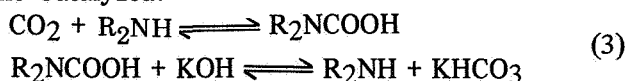
Uncatalyzed:

$$H_2O + K_2CO_3 \rightleftharpoons KOH + KHCO_3$$
$$CO_2 + KOH \rightleftharpoons KHCO_3 \tag{1}$$

Arsenite Catalyzed:

$$2CO_2 + 2KH_2AsO_3 \rightleftharpoons 2KHCO_3 + As_2O_3 + H_2O \tag{2}$$
$$3H_2O + As_2O_3 + K_3AsO_3 \rightleftharpoons 3KH_2AsO_3$$

Amine Catalyzed:

$$CO_2 + R_2NH \rightleftharpoons R_2NCOOH$$
$$R_2NCOOH + KOH \rightleftharpoons R_2NH + KHCO_3 \tag{3}$$

The most significant reaction in an uncatalyzed potassium carbonate solution is the reaction of dissolved

Table 1. Relative packing costs.

Type	Relative Cost per Volume (2 in. Size)
Chemical Stoneware Saddles	1.0 (Base)
Chemical Porcelain Saddles	1.17
Polypropylene Pall Rings (Non-Reinforced)	1.30
Polypropylene Pall Rings (Glass Reinforced)	1.44
Carbon Steel Pall Rings	1.54
304 SS Pall Rings	5.00

CO_2 with hydroxyl ions formed from the available potassium carbonate. The hydroxyl reaction is the significant one since it is believed to be the rate limiting step, governing the overall rate of absorption of CO_2 (1). Commercial units usually employ a promoter which increases the reaction rate, allowing a reduction in the size of the absorption equipment. Typical promoters reported in the literature include:

1. Potassium arsenite (1,2)—Giammarco-Vetrocoke process
2. Diethanolamine (3,4)—Benfield process
3. Amine borates (5)—Catacarb process

Corrosion of carbon steel will occur in potassium carbonate systems unless protected by corrosion inhibitors. Corrosion is particularly severe at high CO_2 loadings, resulting in the predominance of the bicarbonate form in solution. Corrosion inhibitors reported in the literature include:

1. Potassium arsenite (2)
2. Potassium metavanadate (6)
3. Potassium dichromate (7)

Potassium carbonate system designs usually provide a higher level of absorption temperature than typical amine systems, Figure 1. Normal practice is to provide a bulk removal section in the absorber, operating at high temperature, and having little or no cooling of regenerated solution (7). The high temperature favors reaction rate, plus saves investment in heat exchange equipment. An absorber cleanup section is provided, which may operate at a lower temperature to favor reduced CO_2 equilibrium pressure. The cleanup solution may also be regenerated to a lower CO_2 loading than used for the bulk section feed.

Ceramic packing applications

Ten years ago, when we began building hot carbonate systems, ceramics were chosen for packing materials. This was due to a number of reasons:

1. Ceramics had been used in amine CO_2 removal systems previously.
2. Ceramics were thought to have the required corrosion resistance. (Carbon steel packing was thought to be prone to corrosion, and polypropylene had not yet achieved widespread commercial acceptance.)
3. Cost of ceramic packing was as low as, or lower than, the other available packing materials.

Ceramic packing has some considerable disadvantages, as we learned in these early plants. First of all, we found that the specification of ceramic type is important for its resistance to attack by the potassium
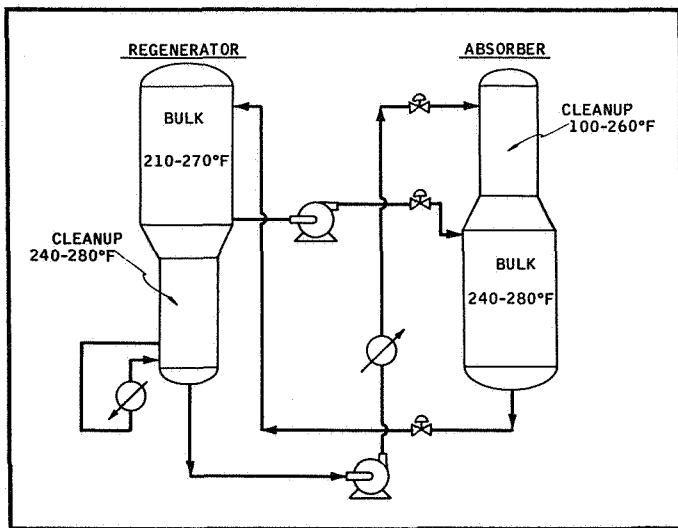
Figure 1.
Typical hot carbonate operating conditions.

carbonate solution. We have experienced serious silica leaching from a type of ceramic referred to as "chemical stoneware." This material is basically a low quality washed clay product which may or may not be glazed (8).

For example, plant A, after about four months of operation, noted a severe rise in pressure drop across the absorber. Circulation rates were continually reduced until the point where the unit was forced to shut down for inspection of the packing. A solid deposit was found at the following locations:

1. In the bottom of the bottom bed of the absorber
2. In the bottom of the top bed of the absorber
3. In the absorber top inlet distributor
4. On the shell side of the lean solution cooler
5. On the shell side of the lean/rich heat exchanger

The deposit was traced to the Raschig rings made from stoneware. The rings, however, showed no evidence of breakage. It seems clear that silica was leached from the packing and then deposited or accumulated in certain parts of the system. The packing was changed to carbon steel.

This silica leaching problem with chemical stoneware packing has been repeated at two other locations. The packing manufacturers now indicate that "chemical porcelain" is the preferred ceramic material for hot potassium carbonate systems. This material is made from a higher purity raw material than chemical stoneware, and reportedly has a higher corrosion resistance and mechanical strength (8).

Even with chemical porcelain packing, we have experienced a number of problems related to packing deterioration. It appears, for the most part, that these cases are the result of packing breakage due to mechanical upsets. For instance, plant B was shut down ten days after initial startup due to severe breakage of the porcelain Raschig rings in the absorber tower. This had been caused by a severe foaming condition which led to tower flooding upsets. This particular unit did not have holddown grids, which fact probably contributed to the magnitude of their packing damage. The packing was changed to carbon steel.

Plant C also experienced a foaming problem on startup, which was accompanied by frequent carryover of solution from both the regenerator and the absorber. Upon inspection, the porcelain rings in the bottom bed of

the regenerator were found to be about 60% smashed, while the upper beds were okay. The regenerator damage was attributed to the flooding upsets. (In this case, a holddown grid had been provided.) The absorber packing was found in good condition, with the exception that a deposit was found in the bottom section which partially plugged the bed. The solids found in the absorber could have been generated from breakage of the packing in the regenerator, but may also have been due to silica leaching as occurred at plant A. The damaged regenerator bed was changed to polypropylene.

Most, if not all, of the reported problems with porcelain packing might be attributed to the flooding upsets. But, these do occur in the operation of hot carbonate units. Foaming is the primary cause. In effect, Figure 2, a system operating in a load region that is acceptable for ceramics is moved into a flooding condition by a foam buildup (8). Although we have antifoam injection facilities, flooding still occurs on occasion.

When tower flooding occurs, the packing is apparently bumped, and if it is ceramic, breakage will occur. Insuring against flooding is not practical, in our opinion. (Even if this were possible, we are left with the question of whether the chemical procelain is truly inert towards silica leaching.) Our company has therefore rejected ceramics for future application in hot carbonate CO_2 removal systems. We do not feel that ceramics can provide a level of reliability which is adequate for present day ammonia or hydrogen units with their many thousands of cubic feet of packing. Our solution has been to seek a packing type which is not susceptible to breakage or erosion due to bed movement.

Carbon steel packing applications

Plant experience with metavanadate containing solutions and ceramic packing showed negligible corrosion of the carbon steel vessel walls. Based on this experience, we began substituting carbon steel packing for ceramics, in order to provide a more rugged packing material. However, a brief look at the corrosion possibilities illustrates the concern one has over using carbon steel packing in systems having a corrosion potential such as this. I estimated that, for a 170 short ton/stream day ammonia unit, the carbon steel vessel and pipe walls amount to 5,000 ft.^{2} of carbon steel surface area, Table 2. The added carbon steel packing constitutes 280,000 ft.^{2}, or, over 50 times the carbon steel surface area. If we had a corrosion rate of 1 mil/yr. (for purposes of illustration), the vessels would contribute about 250 lb./yr. of iron corrosion, which could probably be handled. The packing would contribute six tons of iron corrosion over the same period, and I don't think we could live with that kind of corrosion rate and iron accumulation in the system. We need a corrosion inhibitor that will give essentially nil corrosion rate.

In the use of metavanadate as a corrosion inhibitor, it is necessary to employ oxygen in the process to maintain the activity of the corrosion inhibitor (9). This is a proprietary feature of the Catacarb process. The mechanism for corrosion protection by metavanadate is to form a protective oxide film on the surface of the carbon steel. In the process, the vanadium plus five is reduced. Oxygen has been found effective in converting the vanadium back to the plus 5 valence state, thus insuring its continued availability for forming or maintaining the iron oxide film (9). In commercial ammonia and hydrogen plants, oxygen is supplied by means of air injection.

An example of what can happen if oxygen is not available for maintenance of the metavanadate corrosion

inhibitor can be found from plant reports such as the following: Plant D converted from ceramic packing to carbon steel packing. Previously the unit had operated for five years without corrosion problems. Two months after restart with the new carbon steel packing, formation of a precipitate was noted. This was followed by several flooding upsets and eventually by a pump failure which caused a unit shutdown. The CO_2 system was washed and restarted. Within 12 hr., the precipitate reappeared. In addition to the appearance of the precipitate, the vanadium content in solution rapidly went down and soon disappeared completely. Further additions of inhibitor had no effect in establishing a positive vanadium analysis. The precipitate analyzed 40% Fe, plus had a significant vanadium content. We advised the plant to check their air injection rate, and were told the air meter had been out of service for the previous month. Within two days after assuring a positive air flow, the plant reported a recovery in vanadium level, plus a sharp drop in solids content. Within two weeks after that point, the unit had been cleaned up by onstream filtration with no apparent residual effects of the upset.

This experience has been repeated in a number of plants. In general, once air injection has been resumed, the system can be brought under control and eventually returned to full capacity.

We have established a number of precautions for carbon steel packing applications, based on experience such as the above and based on our theoretical understanding of metavanadate corrosion protection:

1. Protection of carbon steel packing from rust formation in shipment and prior to installation.

2. Low concentration carbonate solution circulation steps prior to startup to remove any residual oil from packing, and prepare packing for startup.

3. Air injection during operation.

4. Provide stainless steel or polypropylene packing as a guard layer where the carbon steel packing may not be fully wetted by solution containing corrosion inhibitor.

Our overall success with carbon steel has been fully satisfactory. Rings removed after three years of service in one plant show no detectable metal loss. However, close attention must be given to system corrosion inhibitor condition.

Propylene packing applications

We frequently use polypropylene packing in conjunction with, or in place of, carbon steel. Polypropylene is of interest for hot carbonate systems which may have higher corrosion rates than obtained with the metavanadate inhibitor, or as the guard layer in a carbon steel system. Our main interest in the early polypropylene applications was to find a packing material which was sufficiently strong to endure operating upsets, and which would also have less sensitivity to system corrosion control than carbon steel.

One of the problems with polypropylene is its limited temperature range. Normal polypropylene packing will soften at about 240°F. We generally specify glass reinforced polypropylene for operation at higher temperatures. This material is acceptable for temperatures up to about 260- to 280°F. Glass reinforcement involves incorporating glass fibers into the polypropylene rings. This increases their cost by about 10%. Areas of the system subject to temperatures about 280°F are packed with other materals such as carbon steel or stainless steel.

Melting of polypropylene has occurred in three of our plants. Plant E had been onstream seven months.

Table 2. Carbon steel surface of a 170 short ton / stream day ammonia plant.

Carbon Steel Surface	lb./yr. Fe*
Vessel + Pipe Wall . . . . 5,000 ft.^{2} 250	
Packing Volume . . . . 280,000 ft.^{2} 12,000	

*Based on 1.0 mil/yr. corrosion rate, for illustration.

Packing was part non-reinforced polypropylene and part carbon steel. It was necessary to undergo a short shutdown for repair of a flange leak in the CO_2 unit. During restart, as the gas rates were increased, excessive pressure drop was experienced across the absorber. After several attempts to raise rates, it was found that maximum gas flow was limited to 30% of design, beyond which severe solution carryover was experienced. Addition of an antifoam agent which had been effective in the past for control of carryover did not help. The unit was finally shut down. Inspection of the beds indicated the polypropylene rings used as a protective guard layer in the absorber had fused into an almost complete plug, leaving only narrow channels for flow. This tower had been provided with a steam connection to purge the tower at shutdown. The steam source was superheated 175 lb./sq. in. gauge steam. This would give in excess of 500°F if the packing becomes dry. We believe that use of this steam purge had melted the polypropylene. A contributing factor may have been an operating temperature level of 270- to 280°F in the absorber; above safe limits for non-reinforced polypropylene. This guard layer has been replaced with stainless steel.

The regenerator packing at this plant operates at 270°F in the lower portion. Although the non-reinforced polypropylene pall rings in the bottom had sagged due to the weight of the packing above, no flow obstructions were noted. The damaged regenerator packing was replaced with glass reinforced polypropylene one year after the upset, and the remaining unreinforced packing is scheduled for replacement with glass reinforced material also. No further fusion problems have been experienced since this failure.

Plant F experienced an upset after four months onstream, which also caused fusion of polypropylene packing in the absorber. Here, the entire absorber was packed with glass reinforced polypropylene. A power failure was experienced, leading to loss of absorber feed gas cooling and solution circulation. Process steam flow continued through the absorber. Due to the loss of inlet cooling, the absorber inlet temperature apparently exceeded the polypropylene fusion limit. This tower was found to have fused polypropylene throughout. It had

Table 3.
Results of lab foam tests on polypropylene packing.

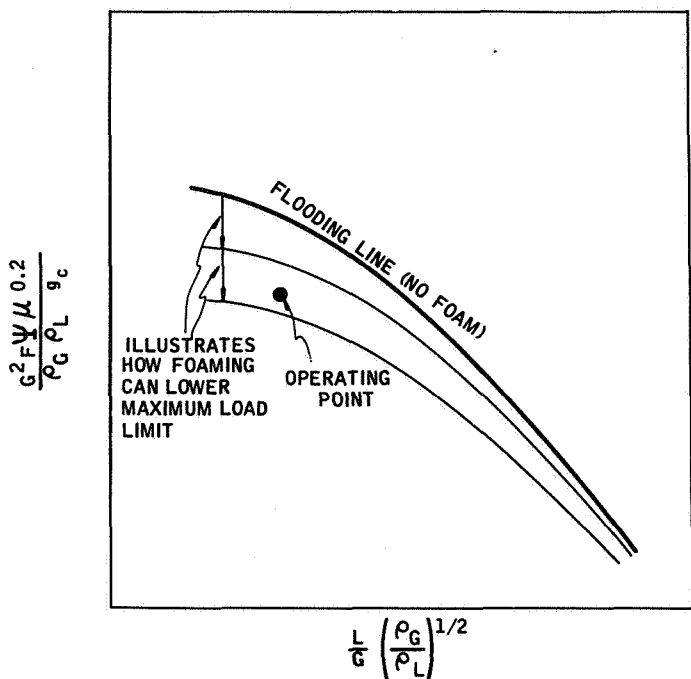| Packing	Initial	Two Day Soaking
Blank Solution	No Foam	No Foam
Unreinforced	No Foam	Slight Foam (10 sec.)
Glass reinforced	Slight Foam (10 sec.)	Stable Foam (30 sec.)
Treated*/Unreinforced	No Foam	No Foam
Treated*/Glass Reinforced	No Foam	No Foam

*Proprietary resin additive

Figure 2. Packed tower flood correlation.

even flowed and then solidified in the rich solution outlet line. Removal of the fused polypropylene was quite a problem! Absorber packing was replaced with carbon steel; polypropylene was left in the regenerator.

We have encountered another problem with the polypropylene packing material that was not attributed to the packing material initially. Each of these plants had an unusually severe foam problem at initial startup. We usually check foam break times by a simple hand shake test—with an acceptable reading being less than 10 sec. foam break. In plant E, our initial foam check on the operating solution indicated in excess of 2 min. foam "break" time! This was clearly a disastrous situation. Gas rate could not be increased over 20% of design without causing severe carryover.

We were unable to eliminate the foam with the antifoam agents on hand. Since this was a remote location, we proceeded with the startup. After several weeks, at reduced capacity with frequent tower flooding and carryover, we were able to obtain a suitable antifoam agent. We also achieved some improvement during this time by circulating a slipstream through a bed of activated carbon.

A severe foam problem was also reported in the initial startups of plants F and G (with polypropylene packing) and again at plant E after the regenerator polypropylene packing replacement. However, plants H and I started up in the same period, with 100% steel packing, and did not experience this foam condition. Lab foam tests were then conducted which pinpointed the cause of the problem, Table 3. The polypropylene packing was contributing a foaming promoter to the solution. Continued use apparently extracts all the foaming agent and eventually leads to a stable operation. However, plant E lost two weeks in the initial startup, plus a methanator catalyst charge due to severe solution carryover. An additional one-day startup time loss was incurred after their polypropylene packing replacement. Plants F and G also experienced significant startup delays due to initial solution foam levels.

Polypropylene itself is not dissolved and is not the cause of this problem. We have traced the foaming to one of the additives used in the manufacture of the resin.

It is obvious from the data in Table 3 that glass reinforced rings are worse than non-reinforced. This has not been explained. It may be due to another additive which reportedly is used to promote good bonding between the glass fiber and the polypropylene.

It is also seen that we have achieved nil foam readings using either unreinforced or glass reinforced polypropylene rings made from a special resin. This resin (Enjay Chemical Co. CD300-MB28) contains a non-foaming agent that was developed by Enjay after we had identified the additive foaming problem. It now appears that we can reduce or eliminate foam induced startup problems with polypropylene packing by using this particular polypropylene resin. Also specified in our packing purchases is no use of quick release molding agents in ring fabrication, so as to prevent a foam-inducement from these additives.

Current status

The following comments summarize our present thinking on hot carbonate system packings:

1. Ceramics are completely rejected, due to lack of reliability that they can withstand the rigors of long-term commercial hot carbonate plant operation.

2. Polypropylene is an acceptable packing material for systems operating below the 280°F allowable temperature limit. Precautions must be taken to insure against temperature excursions. Foam inducement remains as a problem for new packing, unless a non-foam packing type is used.

3. In systems having an inhibitor such as vanadium, carbon steel can provide assurance against damage due to temperature excursions and packing-induced foaming. However, precautions must be observed to guarantee essentially nil corrosion in the system.

4. Finally, we continue to include some quantities of stainless steel in areas where temperatures are too high for polypropylene and where carbon steel cannot be used.

Acknowledgment

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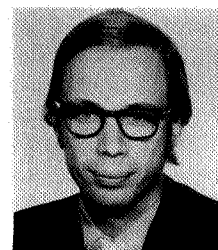
P. A. Ruziska received both his bachelor's degree and master's degree from the Massachusetts Institute of Technology. He has worked for Esso Research & Engineering Company since 1963. At ERE, he has specialized in Agricultural Chemicals processes; and has participated in design and startup activities for most of the Exxon fertilizer projects. He is currently an Engineering Associate supervising a section in the Exxon Chemicals Engineering Department which provides engineering consulting assistance to Exxon's overseas fertilizer companies.