ZIRCONIUM AS A REACTOR LINING

Many difficulties cropped up in using zirconium due to unusual characteristics; successful method has been devised for its use in urea reactor service

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Many problems were associated with the development of a successful method for lining urea reactors with zirconium. This presentation will provide some of the background as well as the progress in this area.

The first claim of U.S. patent 3,236,888 reads: "In the synthesis of urea wherein ammonia and carbon dioxide are reacted under conditions of relatively high temperatures and pressures to form a normally corrosive ammonium carbamate melt in apparatus having surfaces exposed to the reaction mixture, the improvement which comprises conducting the reaction in apparatus constructed in such a manner that the surface thereof exposed to the reaction mixture is zirconium."

Claim 2 cites a urea synthesis reaction temperature of 380 to 450 F. Consider the favorable reaction rates and the favorable equilibrium possible through the use of such temperatures in urea synthesis as compared to the temperature limitation of stainless steel, which is generally accepted to be 375 F.

Vulcan's first endeavor in the urea field was in the early '50's on the basis of a licensing agreement with Inventa A.G. of Lucerne, Switzerland. The Inventa process employed a nominal pressure of 3,000 lbs. with near stoichiometric feed ratios and a separation recycle process utilizing an ammonium nitrate solution to selectively absorb the ammonia in the presence of carbon dioxide.

An improved process

As the competitive pressures from carbamate solution recycle processes increased, Vulcan through its affiliated firm Chemical Processes of Ohio, Inc., undertook the development of improved urea synthesis and recycle processes. To facilitate operation with excess ammonia, in order to obtain higher urea synthesis yields, Vulcan developed a separation process employing concentrated MEA for selective absorption of the carbon dioxide in the presence of ammonia. This process is the subject of U.S. Patent 3,107,149. This was the initial development of what we refer to as the CPI urea process.

To overcome the limitations inherent in stainless steel metallurgy and after extensive research in alternative alloys, CPI undertook the development of a practical means of lining urea reactors with zirconium. The development of such lining would have a collateral benefit of higher allowable operating temperatures and therefore, higher conversion in urea synthesis, resulting in reduced quantities of carbon dioxide to be processed in the selective separation recycle system. You recall we are absorbing the carbon dioxide with MEA.

Many are familiar with the details of these processes and the foregoing was presented only to show the incentive leading to the extensive and expensive effort put forth to develop the zirconium lined reactor. We shall present a brief history of our work with zirconium, our initial failure and our ultimate success.

Zirconium was the candidate

Our selection of zirconium as a candidate for lining the urea reactor was supported by an exhaustive search of published test corrosion data. We then set about investigating the properties and characteristics of zirconium and its alloys with the known producers and the known fabricators and with the foremost metallurgical consultants. These discussions and investigations revealed that there were several problems which would have to be overcome in order to develop a successful liner.

These included special welding procedures, special forming procedures and limitations, and special machining procedures. For example, it was pointed out that inert gas blanketing of the weld would be necessary to obtain a ductile weld. However, the details of such procedures must be based on experience. Therefore, CPI and Vulcan undertook a welding development and training program to qualify welders for the fabrication work.

During efforts to qualify fabricators for the forming of specific required shapes, many of them subsequently declined to participate in the fabrication of the equipment because of problems such as cracking during forming of zirconium plate.

Pyrophoric nature a problem

During machining of lens rings, valve parts, etc., we learned that special cutting speeds and feeds, and tool angles are required. An additional problem is the pyrophoric nature of the machining chips.

After developing proper welding, forming, and machining procedures, the concept of a lining design was considered in detail. Of the three methods conceived, only the method, later proven unsuccessful, seemed feasible at the time because of limited fabrication experience. Three methods were considered -- first, a shrunk-in liner employing the thermal shrink fit methods of Struthers Wells; second, a loose bag or thimble liner; and third, a welded in place liner.

The latter method was selected initially for lining the urea reactor originally installed at Premier Petrochemical Corp., Pasadena, Tex. Half cylinder sheets were rolled and pressed in place with large brake shoes. Straps were placed over the butt joints and welded with purging only from the welding side. We relied upon the fit of the plates and the straps to preclude entry of reactive gases into the weld from the back side. This method of welding had proven successful in bench scale work, as proven by X-ray and bending tests. However, the in-place fabrication would not permit X-ray inspection of the zirconium weld.

An initial failure

A dye-check of every inch of welding did not reveal any evidence of porosity or poor welding quality. This liner subsequently failed in service at the welds of the straps allowing the urea and carbamate melt admission outside the zirconium liner. This initial failure, of course, immediately directed our attention to alternative zirconium liner designs.

At the time of this failure, reactors for three other plants were on order, each on the basis of the pressed-in-place welded liner. Immediately redesigns were undertaken and a loose liner with a pressure equalizing purge between the liner and the vessel shell was employed as an alternative design. Such purged loose liners were installed in the new plants of Cominco Ltd., Calgary, Alberta, Allied Chemical, South Point, Ohio and Nipack, Kerens, Tex. At the same time development work was undertaken with Struthers Wells Corp. to develop a method for fabrication of a zirconium lined vessel using their thermal shrink fitting procedures.

The thermal coefficient of expansion of zirconium is approximately 60% that of steel and in order to minimize the tensile stress in the zirconium liner when the vessel is at operating pressure and temperature, it was decided to shrink a steel shell onto the zirconium liner and place the liner under sufficient compression when cold, that at operating pressure and temperature the zirconium liner would be in a near neutral condition.

The method was successful

By extrapolating fabrication experience with stainless steel, it was predicted that such a technique would be successful. Nevertheless, test sections three feet in diameter were assembled as a demonstration. These were successful.

Struthers Wells and Vulcan continued their collaborative effort and fabricated the first shrink fit zirconium lined vessel for Mississippi Chemical at Yazoo City, Miss. as a part of their recent plant expansion. This vessel has been placed in service and has been in operation since May, 1966. The reactor has been pressure cycled several times and the liner has been inspected two times. There is no evidence of difficulty with the liner.

In summary, Vulcan has undertaken liners of zirconium using three different methods.

The first method, a pressed-in welded in place design, proved unsuccessful due to the mechanical failure of welds.

The loose liner method, although it requires a purge pump system, has proved to be a successful method. It is available as a method of lining existing urea reactors. To the extent that the higher operating temperature could be of benefit in existing reactors, the loose zirconium liner would result in additional urea capacity.

The final, and presently preferred, method for new facilities was the thermal shrink fit method. Because of the higher temperature, and therefore higher conversions and higher reaction rates and thus lower reactor volume, we find that the zirconium lined reactor system is only slightly more expensive than the usual stainless steel system. The advantages of higher conversion of carbon dioxide, reduced recycle system utilities, operating simplicity, lower maintenance, etc. more than offset the incremental cost of the zirconium system.

Before closing I would like to bring this up-to-date historically. In April, 1964, Allied Chemical Corp. acquired ownership of the CPI urea process, including the zirconium developments and the concentrated MEA recycle system. Under the CPI-Allied relationship, Vulcan is authorized to license the process which is now commonly referred to as the CPI-Allied Chemical urea process.

Discussion

Q. Does zirconium suffer from hydrogen embrittlement at all if hydrogen is absorbed by zirconium?

Dick Dopp (Vulcan Cincinatti): I think this is a two-part response in that under the proper conditions it definitely does. In the applications wherein we have used it, we have experienced no such problems.

Q. Do you take care to avoid embedded iron or foreign materials in the surface of your liner before commissioning the liner? Do you pre-pickle or clean or take other precautions to avoid a situation in which less noble metallic materials are embedded in the surface of your liner.?

Dopp: As a pickling operation, no we have not. But with titanium or zirconium, you are probably familiar, you have a clean room normally in which it is worked. All the working conditions are kept as clean as possible. The working space is air conditioned. This kind of precaution is observed.

Q. There is also one other alternative to the sequence of choices that you described that you didn't apparently explore and that is to use a liner of some body or integrity in its own right, that is ¼" or something of this sort with a vented steel support shell as an alternate piece or equalizing purge. Did you consider this as a possibility and reject it as being undesirable or is it something that you had other reasons for not wanting to explore?

Dopp: I have to say that I haven't personally considered it.