Recent Developments in Welded Refinery Equipment

The field of petroleum refining used to be a series of simple physical processes, but, in recent times and increasingly today, it has become a series of complex chemical processes. Recent developments require the petro-chemist to use not only extraction methods other than absorption and distillation, but also chemical and catalytic reactions involving many reagents other than the natural hydrocarbons.

New equipment has had to be developed for this new petroleum technology. This paper will describe some of the recently developed equipment. There will also be presented some of the details of construction, with particular reference to the materials used and the various welding processes for joining these materials.

The separate types of equipment in a modern refinery are too numerous to treat individually. Furthermore, much repetition would occur were we to consider refinery equipment in terms of refinery processes, such as alkylation, polymerization, thermal and catalytic cracking, and so on. The most interesting aspects of recently developed equipment may be summarized as due to the increasing demands for:

1. Higher operating temperatures.
2. Higher operating pressures.
3. Larger pressure vessels.

These four topics will be discussed separately, although all the conditions represented often occur together.

Higher Operating Temperatures

Operating temperatures of 750 degrees F., and upward to 1100 degrees F., are more and more frequently encountered. Thermal cracking, for quite a few years past, has employed temperatures from 850 to 1000 degrees F. But some catalytic cracking processes now require operation at over 1000 degrees F. At these temperatures metals are actually red hot. And for operation at red heat, the selection of materials and the design of equipment must take into account the following factors:

A. The high temperature strength of the material (resistance to creep).
B. The possibility of temperature embrittlement.
C. The accelerated corrosion rates at high temperatures.

In meeting the three conditions A, B and C, present...
when high temperature is encountered, the materials used greatly influence design of the equipment. Following are a few examples of design and fabrication considerations, as related to the material selected.

Straight carbon molybdenum steel (A.S.T.M. A-204) may be selected for creep strength (factor A), but it may not satisfy factors B or C. In other words, although the creep strength of carbon-Molybdenum is about twice that of carbon steel at 1000 degrees F., operating conditions at this temperature may induce temperature embrittlement, or the carbon-molybdenum steel may offer inadequate resistance to corrosion.

It has been found that the addition of chromium, even in relatively small amounts, to carbon-molybdenum steel materially reduces the risk of temperature embrittlement, and may add to the creep strength. As little as 1.25 per cent chromium with 0.3 per cent molybdenum may be used to satisfy factor A and factor B. But this small amount of chromium usually is not sufficient to improve the corrosion resistance very much.

The high temperature corrosion problem alone has three distinct elements: First, atmospheric corrosion, which at lower temperatures is almost no problem at all; second, the special type of heat corrosion encountered in those cases where equipment is direct-fired or in contact with hot furnace gases; and third, the corrosion due to the process fluids. A further discussion of the corrosion problem is included in the latter part of this paper.

When creep and embrittlement and corrosion are all expected, the economic solution is sometimes found in the use of plain carbon-molybdenum steel for the pipe or vessel wall, to provide the necessary creep-strength, plus the use of a liner of high-alloy material to resist the corrosion or embrittlement that the process fluid would otherwise cause. The various forms that the liner may take, such as cladding, plating, or separately attached lining, will be discussed more in detail.

It is indeed fortunate that welding processes and techniques have been well developed for materials other than plain carbon steel. It is by virtue of the versatility of welding that the alloy or composite materials so often necessary for high operating temperatures can be fabricated in the size and shape necessary for almost anything from a simple pipe to a complicated heat exchanger. Moreover, welded attachment of alloy linings, whether by fusion plug welding or by resistance spot welding, is often the most economical method of providing such linings. And when clad material is used, though it may be costly, the cost is minimized if fabricated by proper welding methods.

Equipment for high operating temperature frequently involves complex combinations of low and high alloy materials. Accordingly, at this point we will temporarily postpone discussion of topic No. 2, high pressures, and topic No. 3, large vessels, and will mention some of the methods of welding alloy materials and composite materials.

It has been found that electric fusion welding is entirely satisfactory for most of the low-alloy steels, if proper welding rods are selected, and the special preheating precautions necessary in some cases are observed. There is one low-chrome alloy, however, that has been quite troublesome. It is the type 301 or type 502 stainless commonly called 4-6 per cent chrome. This alloy has a marked tendency to air-harden in the temperature range around 500 degrees F., and any welding process employed is bound to create a temperature gradient extending into this air-harden range, unless something is done about it. What usually has to be done is to maintain a preheat temperature above the air hardening range and to conduct all welding operations at or above, say, 500 degrees F. Furthermore, the anneal necessary to stabilize the properties of this alloy must follow the welding without loss of the preheat temperature. In other words, to avoid the air hardening effect which may cause embrittlement or actual cracking of the material or the welds, a very elaborate setup is required, and much discomfort is involved for the welding operator. Because of these conditions, it is sometimes more practical to use the more expensive but easier to weld higher-chrome alloys, such as 11-13 per cent chrome, even though a lower chromium content would satisfy the operating temperature or corrosion problem.

The welding complications just described are often alleviated by the use of good old-fashioned acetylene welding, with its wider heated zone in the vicinity of the joint, but this process does not provide much of a protective envelope while the weld is being made. The atomic-hydrogen process is often superior, because it combines the ability to create a broad heating band, with an almost perfect reducing atmosphere (the hydro-
a. Detrimental dissolving of excess carbon from the carbon steel (or the dissolving of carbon steel itself) into the higher-alloy steel, or

b. The contaminating effect of some of the alloying constituents migrating into the weld joining adjacent portions of the parent metal.

In case (b), the effect is usually bad because of the formation of an imperfect alloy in the weld itself, which may seriously weaken the joint. It is obvious that the strength of the vessel or pipe is dependent upon the joint because the strength of lining or cladding is seldom, if ever, taken into account in the design. The pressure-vessel codes allow no credit for liners or the alloy portion of clad plates, in computing the strength of the vessel.

In case (a), the detrimental effect is primarily due to carbon pick-up spoiling the anti-corrosion properties of the alloy, or secondary effects such as checking.

LOW-TEMPERATURE OPERATIONS

While on the subject of temperature-effects, and before proceeding to discuss high operating pressures, we should mention the present status of low operating temperatures in today's refineries. Although alkylation processes, and cold acid treating, and solvent extraction, all commonly use refrigeration, the low operating temperatures have not become materially worse, from a design standpoint, than those low temperatures encountered some 10 years ago in solvent dewaxing. At that time, investigations were made of the special design problems incidental to low operating temperatures (around 100 degrees below zero Fahrenheit) where the main problem was that of impact strength, and where the generally acknowledged solution was the use of nickel steel, contain-
ing from two and one-half to four per cent nickel. Such steel was found to be weldable, and is still commonly used for low temperature applications. Now, still speaking of cold temperatures, we can only go down 460 degrees below zero F. and no lower. Up toward the other end of the thermometer, however, even 1000 degrees F. may not be the limit. According to one authority, thermal polymerization may require over 1100 degrees F., and tomorrow the industry may need to go still higher.

HIGH PRESSURE AND SUPER-PRESSURE

To apply the term “high pressures” to working pressures near 400 p.s.i. is almost obsolete. Nowadays, one thinks of pressures from 750 to 1500 p.s.i. as high pressure, although the limits are very indefinite. Where high pressure ends and super-pressure begins is an open question. One authority considers pressures over 100 atmospheres, roughly 1500 p.s.i., and up to 50,000 p.s.i. to be super-pressures. Another states that the best definition is that we are dealing with super-pressure if the cylinder wall thickness exceeds 10 per cent of the diameter. Suffice it to say that pressures from 500 to 1500 p.s.i. are becoming quite common, and that full scale refinery operations at 3000 p.s.i. are not unheard of, and that there is at least one well-developed line of laboratory and pilot plant equipment for up to 50,000 p.s.i.

Even for the moderately high pressures around 1000 p.s.i., the design of equipment must take into account many more factors than when dealing with only 100 p.s.i. The designer of high-pressure equipment must consider:

1. Alternate materials; carbon steel or high strength alloys.
2. Size and shape factors; see Fig. No. 1 and below.
3. Type of construction:
   a. Rolled and welded; single-plate wall or multiple layers.
   b. Seamless: forged, drawn, or case, or bored from solid.
   c. Combinations of a and b, such as welded attachments on a seamless shell.

These factors will be considered in the order presented above.

Selection of material for high-pressure construction is almost always determined by making an economic balance between massive carbon steel and expensive alloy steel. This economic balance, however, involves more than simply material costs and fabrication costs; the availability and suitability of the material must be considered also. As in high-temperature design, the action or reaction of the process fluid on the material is often of supreme importance. If high pressure is accompanied by high temperature, all of the factors under each of these headings must be considered fully. Fortunately, the alloy materials outlined under the preceding discussion of high temperature have higher-than-ordinary tensile strength, and hence, are advantageous in meeting the requirements of high pressure. For example, carbon-molybdenum steel, often selected for high temperatures because of its better creep strength, is available in three grades—A, B and C, and has minimum (cold) tensile strengths respectively of 65,000, 70,000 and 75,000 p.s.i. One method of treating the
problem is to make the main wall of the vessel of the strongest suitable inexpensive material, and employ a liner to meet the heat or chemical corrosion problem. For instance, a fusion welding piping assembly for pressure at high temperature (the pipe being fabricated by rolling and welding clad plates) has carbon-molybdenum base metal with 18-8 stainless cladding, the carbon-molybdenum to provide strength at high temperatures, and the stainless to provide resistance to corrosion by the flowing catalyst.

When high pressure alone is being considered, uncomplicated by high temperature or severe corrosion, the lowest cost high-strength steels are carbon-silicon (A.S.T.M. A-94, A-201 and A-212) or carbon-manganese (A-225). Until sidetracked by the advent of the present war, the low alloy steels known as Corten and Mayari-R also provided low cost high strength materials, both easily workable and easily weldable.

In high-pressure vessels, shape and size are not mere factors of convenience. The process requirements for size may have to be modified to permit selection of an economic design. The cost per cubic foot of capacity becomes a matter of much money when pressures of 500 p.s.i. and upward are encountered. Small diameters minimize the cost, but some reactions, particularly catalysis, may require as large an area or volume as possible; hence the factors of size, shape, material, construction, and operation must be balanced.

The type of construction to be employed in a vessel for high pressure will determine to some extent what materials may be employed. For instance, in seamless forged, or bored-from-the-solid, or cast vessels, high strength may be provided by high-carbon content alone. The use of high carbon, however, may preclude the possibility of making any attachment by welding. As has already been pointed out, carbon-molybdenum steel, carbon-silicon steel, the low-chrome steels, and the stainless steels, whether used as the main vessel-walls or as liners, can readily be welded.

Welding also has made possible some very interesting combination designs for high pressures, such as long-stroke pumps made by welding two or more forged steel parts together; the welding of the outer barrels for Hydropress pumps; and the familiar examples of welding into multiple-layer vessels, an example being a vessel in hydrogenation service at high temperature; it is about 1000 degrees F. The required stress relief at temperatures somewhat lower than the 1100-1200 degree range generally recommended is feasible, but a much longer time is required—at 1000 degrees F., about 10 times as long as at 1100 degrees F.

Case IV:
A typical catalyst regenerator operates at 1100 degrees F., is 42 inches in diameter by 35 feet shell height, and has a 90-degree cone bottom. The top is a practical combination of cone and dome, having about two-thirds composed of a 90-degree cone, and the upper one-third bridged over with a portion of a sphere. Just a chamber, having no internal parts, but being constructed of one-inch plate for the shell and one and one-quarter inch plate for the
The gargantuan catalyst equipment described in joined by welding in the field, usually before erection. Often building supersize vessels are many. Plate thickness over one inch. For connection and transporting to the site. Even so, rather than welding in the field means that every pre-connection involves all of the problems previously discussed under the topic of high temperature. The men and materials during construction, but also the safety of operation of the finished vessel. Safety of operation of the finished vessel.

Case V:

Typical catalyst hoppers are 30 or 32 feet in diameter by about 80 feet high overall, and have conical bottoms and full hemispherical top heads. Design is for five p.s.i., working temperature is 650 degrees F. As in the case of very tall fractionating towers, the shell thickness varies from top to bottom. These hoppers are about one-half inch thick at the top and each course of shell plate, proceeding downward, is one-sixteenth- to one-eighth-inch thicker, making the bottom course about one inch. One hopper weighs over 250,000 pounds when empty.

Case VI:

Although standard A.P.I. storage tanks continue to be generally used, with cone roofs or floating roofs, for storage of low vapor pressure fluids, there has been an interesting development of containers for high vapor pressure fluids. Large spheres and spheroids are suitable for pressures from 10 to 100 p.s.i., and volumes up to tens of thousands of barrels. Large diameter vertical pressure containers have been used, and supersize horizontal cylindrical tanks are now being constructed for pressure storage of liquids. An example of a recently developed special design of horizontal pressure tank of large capacity is located in southern California. It is 38 feet in diameter by 114 feet long, for a working pressure of 60 p.s.i. The novel feature is the method of support. Instead of two piers or cradles, which would require two ring girders to maintain the tank round at the points of support, and would involve sliding bearings or rockers at one end to allow for expansion, a transverse central support is used. The ring girder at this point is inside of the tank shell, and so the whole thing looks like a blimp almost floating in mid-air. The advantages, of course, are freedom to expand and contract, or to curve under the differential heating of the sun's rays, and, it is claimed, ease of field erection resulting in low cost per gallon of contents. In comparison with spherical containers, the cylindrical type is not at such a disadvantage as many believe. The mere fact that for a given pressure and diameter a sphere needs to be only half as thick as the cylinder does not mean that the weight or cost of a sphere will be half that of a cylindrical tank for a given capacity. (See Fig. No. 1.)

The transportation and construction problems in building supersize vessels are many. Supercracker sections, to be connected, are sometimes 400 feet long. The gaggantuan catalyst equipment described in case-histories III, IV and V obviously cannot be shipped even partly assembled. Erection becomes a matter of assembling, plate by plate, the individual pieces after prefabrication and transporting to the site. Even so, rather heavy lifts are involved in building those vessels with plate thickness over one inch. For example, a one-and-one-half-inch plate eight feet wide by 30 feet long weighs 15,000 pounds, and such plates must be lifted to fantastic heights to assemble a catalytic reactor, say, on the 14th floor of the building. Field welding of these vessels, as is evident from the construction details given in the case histories, may involve all of the problems connected with welding of composite materials as previously discussed under the topic of high temperature. Doing such welding in the field means that every precaution must be taken to insure not only the safety of the men and materials during construction, but also safety of operation of the finished vessel.

CORROSION AND ABRASION

All of the "old" corrosion problems are still with us, and a host of new ones are at hand. As has already been mentioned, any or all corrosion is aggravated by the higher temperatures of operation. Many of the old corrosion problems were adequately solved by simply providing extra metal for corrosion allowance. Most of the new corrosion problems are not solved that easily. The prevention of chemical attack, of heat or stress corrosion, of embrittlement, and of hydrogen-penetration, may require the most expensive materials and the best fabrication knowledge available. Do not expect this brief study of equipment to answer all the new corrosion questions. Just a few of the things that are being done will be reviewed; and some of these things are only trial attempts to find out the answers.

The use of substances heretofore foreign to refinery operations is compelling the careful adaptation of materials equally foreign to the usual refinery experience. Here are a few examples:

**Hydrochloric acid** may occur in such form and such concentrations that only a very high alloy like Hastelloy will endure. In one such case, a liner of Hastelloy is installed in the tower section and bottom cone of a tower, and also within the necks of certain nozzles. Attachment is by plug welding, except that small diameter nozzles are of solid Hastelloy. Because this alloy costs several times as much as 18-8 stainless steel, its use is generally limited to zones of expected corrosion where nothing else will do. In welding Hastelloy the welds tend to be porous; remelting of the weld in a carefully controlled atmosphere boils out the porosity and gives a smooth bead. The atomic-hydrogen arc is especially well suited to this "sealing" operation, but the acetylene flame also can be used successfully.

**Hydrofluoric acid** is another of the newcomers. When most of us were first introduced to hydrofluoracetic, we learned that its salient property was that it couldn't be kept in glass bottles, and this property has earned for HF an undeservedly bad reputation for supercorrosion. Just like concentrated H2SO4 and anhydrous HCL, according to C. M. Fehr, anhydrous HF can be tolerated by any good steel. By contrast, at concentrations over 65 per cent it attacks lead rapidly. Welded or cast steel equipment, therefore, may be used when the acid is known to be anhydrous, or nearly so.

**Ammonia** is not only a refrigerant but also a reagent or catalyst, as in modern toluene plants. Some designers or users may need the reminder not to use brass or copper in ammonia's presence, not even to braze a cracked compressor head, if the ammonia is to be held.

**Hydrogen sulfide**, no newcomer to the group of corrosion problems, nevertheless brings new headaches when it appears in some of the new processes. In one case where H2S was present at a temperature of 900 degrees F., the piping and accessories had to be stainless steel, 18-8 with three per cent Molybdenum. In another case, this insidious compound H2S had to be removed because it acted as a "poison" spoiling the action of phosphoric acid as the catalyst in making polymer gasoline. In absorbing or otherwise separating H2S from a gas stream, a weak acid may be formed and lead lining (if temperature permits) may be needed to avoid this corrosion.

The non-ferrous materials, notably copper and Everdur, Monel, Inconel, and nickel, are becoming increasingly useful in meeting new conditions of corrosion, or in some cases conditions requiring non contamination of the products by iron. Fortunately, the chemical process and food industries in solving similar problems caused the development of dependable methods of work-
ing these non-ferrous materials into exchanges, pressure vessels, etc. This "know how" will be very useful to the new petro-chemical industry. Some examples of non-ferrous equipment are: copper and Everdur reaction-chambers, nickel salt-handling equipment, Monel or Incoloy evaporators, and solid Hastelloy (nearly non-ferrous) for plastic-compounding.

Many of the newer cracking and reforming operations involve dehydrogenation. In these, as well as in the direct hydrogenation process, the presence of free hydrogen may cause the phenomenon known as hydrogen-penetration. This causes progressive deterioration of the steel and to date, I am told, no fully satisfactory remedy has been found. Vessels have been made with walls twice as thick as would otherwise be required, but still the hydrogen seeps through.

Now a word about abrasion. Without referring too specifically to the mechanism of the several new catalytic processes, it may be said that at least two of them use finely divided solids as catalysts, and these fine solids are caused to flow in suspension in fluids. During this flow, and in subsequent separation (in one process), the solid particles act abrasively. Equipment handling this mixed flow condition may be either of abrasive-resistant material like the workable low-manganese alloy steels, or, the anti-corrosion claddings or liners, by virtue of their generally better physical properties, hardness and tensile strength, may offer long enough economic life. If temperature permits, one should not overlook the fact that rubber linings are often resistant to both abrasion and corrosion.

CONCLUSION

The development of the new applied science of petrochemistry is just beginning. As new processes, new reactions, new catalysts are discovered, and new products are developed from petroleum there will be more new equipment—perhaps unlike any we have yet seen. That is the only conclusion with which this article can end.

Photo on page 13 courtesy the Lummus Co.

Benjamin Franklin (Continued from Page 9)

ments of a huge and thus far completely unexplored field, and his wrong steps give him opportunity to show his greatness by the way he goes to work to discover and to admit his error. Thus, he writes as follows:

"Query, Wherein consists the difference between an electric and a non-electric body?"

"Answer, The terms electric per se, and non-electric, were first used to distinguish bodies, on a mistaken supposition that those called electric per se, alone contained electric matter in their substance, which was capable of being excited by friction, and of being produced or drawn from them, and communicated to those called non-electrics, supposed to be destitute of it: For the glass, etc., being rubbed, discover'd signs of having it, by snapping to the finger, attracting, repelling, etc. and could communicate these signs to metals and water.—Afterwards it was found, that rubbing of glass would not produce the electric matter, unless a communication was preserved between the rubber and the floor; and subsequent experiments proved that the electric matter was really drawn from those bodies that at first were thought to have none in them. Then it was doubted whether glass and other bodies called electrics per se, had really any electric matter in them, since they apparently afforded none but what they first extracted from those which had been called non-electrics. But some of my experiments show that glass contains it in great quantity, and I now suspect it to be pretty equally diffused in all the matter of this terraqueous globe. If so, the terms electric per se, and non-electric, should be laid aside as improper; and (the only difference being this, that some bodies will conduct electric matter, and others will not) the terms conductor and non-conductor may supply their place."

Without doubt the most profound paragraphs in all of Franklin's letters are the following, written in 1749:

1. The electrical matter consists of particles extremely subtle, since it can permeate common matter, even the densest metals, with such ease and freedom as not to receive any perceptible resistance.

2. If any one should doubt whether the electrical matter passes through the substance of bodies, or only over and along their surfaces, a shock from an electrified large glass jar, taken through his own body, will probably convince him.

3. Electrical matter differs from common matter in this, that the parts of the latter mutually attract, those of the former mutually repel each other. Hence the sparing difference in the stream of electrified effluvia.

4. But though the particles of electrical matter do repel each other, they are strongly attracted by all other matter.

5. From these three things, the extreme subtlety of the electrical matter, the mutual repulsion of its parts, and the strong attraction between them and other matter, arise this effect, that, when a quantity of electrical matter is applied to a mass of common matter, of any bigness or length, within our observation (which hath not already got its quantity) it is immediately and equally diffused through the whole.

6. Thus common matter is a kind of sponge to the electrical fluid. And as a sponge would receive no water if the parts of water were not smaller than the texture of the sponge; and even then but slowly, if there were not a mutual attraction between those parts and the parts of the sponge; and would still imbibe it faster, if the mutual attraction among the parts of the water did not impede, some force being required to separate them; and fastest, if, instead of attraction, there were a mutual repulsion among those parts, which would act in conjunction with the attraction of the sponge. So is the case between the electrical and common matter.

7. But in common matter there is (generally) as much of the electrical as it will contain within its substance. If more is added, it lies without upon the surface, and forms what we call an electrical atmosphere; and then the body is said to be electrified."

In these paragraphs Franklin states with great succinctness what later became known as the Franklin one-fluid theory, and after 1800 was known as the electron theory. In his day and for 150 years thereafter it received very scant consideration in the old world, and the so-called two-fluid theory of Aepinus, put forward a little later, was universally taught in textbooks the world over up to the triumph of the electron theory in 1897 under the active leadership of J. J. Thomson, who himself pointed out that this electron theory was in essential particulars a return to the theory put forth by Franklin in 1749. For Franklin's electrical matter consisted of extremely subtle mobile particles (now called negative electrons), which in order to make matter exhibit its common or neutral properties had to be present in each kind of matter (we now say in each kind of atom; but the atomic theory had not been formulated in 1749) in a particular number, an increase in which number made it exhibit electrification of one sign, a decrease, an electrification of the opposite sign. In Franklin's theory only one kind of electrical matter was mobile, the other sign of electrification appeared when the mobile kind was removed so that it could no longer neutralize the effect of the opposite kind which inhered in the immobile part of the matter (i. e., in the nucleus).

The Franklin theory was mathematically identical with the two-fluid theory, but while the former was a definite and profound physical theory the latter was a hold-over from medieval mysticism. It came from the