60 Years of Petroleum & Petrochemicals Industry Refractories History & Opportunities for the Future (You Snooze-You Lose!)

Crude oil refining has been ongoing for many years. In early days, the basic process for refining entailed boiling crude oil to the point that it would evaporate and then distilling it. Since crude oil is composed of hydrocarbon molecules of varying chain lengths, the longer chain molecules have the higher boiling points. When a crude oil is heated and then cooled, the longer chain molecules condense or liquefy at the higher temperatures with progressively lower condensation temperatures with shorter hydrocarbon chains. From these fractions come various petroleum products from a light, single molecule of methane to jet fuel, kerosene, gasoline, diesel fuel to the heavy, longer chain molecules that compose asphalt. The more profitable fractions of oil are the lighter, shorter chain molecules altered for good ignition in.

The simple refining of oil requires significant heat input to boil and evaporate crude oil. This was accomplished by refractory lined rectangular or cylindrical type heaters firing oil, natural gas or refinery gases. Oil was heated by circulating through alloy metal tubes in the furnaces. Normal furnace temperatures range from 870°C to 1090°C (1600 to 2000°F) in radiant sections, from 900 to 500 in convection sections and then the fluegas exits the furnace into breechings, ductwork and stacks. The key concern in a furnace is to transfer heat as efficiently as possible to the oil in the tubes. Metal shell temperatures normally operate at about 180°F. Some units today also re-circulate the fluegas off the furnace and heat the combustion air going to the burners.

Initially, heaters were lined with firebricks backed up with some kind of a fibrous insulating material such as mineral board. Field mixed insulating (about 50 lb/ft^3) refractory castable was the second generation of refractory lining systems for heaters. Some of the original castable linings, installed 40 or 50 years ago are still in place and performing well. Field mixed refractories have given way to proprietary castable linings that are much more consistent. Installation procedures vary for these types of products from casting to pneumatic placement. One of the real benefits of using calcium aluminate cement bonded castables is the tendency of the basic nature of the refractory neutralize sulfuric acid that condenses in linings because of the levels of sulfur in furnace fuels fired. In recent times, the tendency has been away from firing high sulfur containing oil toward the use of lower sulfur containing refinery fuel gases and natural gas.

Silica (SiO_2), Alumina (Al_2O_3) based amorphous ceramic fiber, invented in the United States in the middle 1950's has become, a popular choice for heater linings because of its very low coefficient of thermal conductivity which led to lighter, thinner linings as compared to brick and insulating castable linings. The amorphous ceramic fiber is inert to sulfur containing compounds that condense in the lining and on the metal shell and significantly corrode the metal shell. In the past, when furnaces fired bunker C oil containing high sulfur and significant levels of alkalis such as sodium and vanadium, they hot face of the ceramic fiber was attached by the alkalis while the metal casing was corroded by the condensation of sulfuric acid on the metal shell. Because of the alkali attack, more dense refractory castables are used.

When sulfur is in the fuel fired, a bitumen or coal tar epoxy should be used to coat the metal casing to minimize casing corrosion concerns. In the past and even in some instances today, metal foil vapor stops have been placed with the layers of ceramic fiber blanket at an isotherm which is slightly above the acid dewpoint which is about 350°F. This foil vapor barrier must be made of stainless steel, not aluminum, since aluminum will be affected by heat. The effectiveness of the vapor barrier is questionable since it must be overlapped and the support studs for the ceramic fiber must penetrate the barrier to support that lining.

Ceramic fiber linings are designed to be installed as layers of blanket supported with studs and twistlock clips. Ceramic cups are also used to hold the blankets onto the studs with ceramic mortar filling the cups after the attaching to the studs. Fiber folds or wraps, often called diapers, are also used to protect the twistlock clips from direct heat.

For the burner tiles, phosphate bonded monolithic refractories that can be heated rapidly and have excellent resistance to temperature and thermal shock are used.

Although fired heaters are the backbone of the refinery, refractory technology for this equipment has not progress in recent history. Heater refractory usage is often very competitively bid.

One problem/opportunity that has been known to plague insulating castable refractory linings for fired heaters is alkali hydrolysis. Alkali hydrolysis of refractory linings involves the presence of three elements in a warm, humid environment. In the presence of moisture, carbon dioxide and alkali the alkali catalyzes the reaction between the carbon dioxide and calcium aluminate cement to form an expansive calcium carbonate which disrupts the cement bonding. Lining surfaces crumble over time if not dried out promptly or placed into the service. From examining the three necessary ingredients for the reactions, humidity and CO_2 are obvious provided by the atmosphere, but one wonders the source of the alkali which must be present for the reaction to occur. Investigation shows that a significant amount of potassium contaminant is present in perlite, a very low density insulating aggregate used to impart the insulating properties of insulating castables used in fired heaters. Repair of alkali hydrolysis affected castable linings can be expensive and very inconvenient. To thoroughly understand alkali hydrolysis and eliminate it or learn how to manage it so as to minimize the effect would be a welcome refractory lining advancement.

When heated the shorter chain molecules vaporize at lower temperatures while the vaporization temperature for the longer chain molecules is higher. While fired heaters and unlined fractionation columns for separating the various fractions of hot crude into useful products and heavier, longer chain fractions continue to be a mainstay in refineries, recent developments in the last about 71 years have sharply improved the yield of a barrel of crude oil. With the splitting of the long chain, heavier fractions of the crude into shorter chain, more useful fractions, one barrel of oil can be increased in volume yield by 25 to 40%. In the late 1930’s and early 1940’s came the discovery of the “catalyzed cracking” of heavier, longer chain oil molecules into the shorter, more useful molecules. This catalyzed cracking utilizes a sintered powdery catalyst substance composed primarily of silica and alumina (SiO_2 & Al_2O_3)

and occurs at temperatures between 900 and 1000°F. In order to commercialize this catalysis process, a number of issues had to be addressed. Of course the feed stock for such a process could be heated to the desired temperature using fired heaters. The following list provided the early most pressing issues/opportunities:

1. How to intimately blend the feed stock with the catalyst in order to accomplish the desired cracking.
2. How to effectively separate the catalyst from the cracked product.
3. How to regenerate the catalyst after it had been coated with coke and residue after the cracking process had occurred.
4. How to effective separate the regenerated catalyst from the gases that had been burned off the catalyst during the regeneration phase.
5. How to transport the regenerated catalyst back so that it could again be blended with the feed stock.
6. How to insulate the process so as to protect the metal from strength loss at high temperatures.
7. How to accommodate the thermal expansion of the equipment used facilitate this process.

With all of the above issues have come continuous significant opportunities in the last 60 years for a continuous string of developments in refractory materials installation techniques, product properties improvements, anchoring arrangements for holding the linings in place, test procedures to facilitate continuous refractory improvement, and quality control/assurance information.

Other issues which present opportunities related to the refining of oil are gas cleanup and additional removal of catalyst from combustion air and cleanup of the air that will be released to the atmosphere. Some heavy crudes containing significant levels of sulfur that must be removed from feed stocks either before or after the refining process is completed. De-salters are also needed to remove the salt that can be mixed with crudes that are imported in oil tanker

In 1942, Exxon designed and built the first fluidized bed catalytic cracking unit (FCCU) that facilitates the cracking of crude by designing the equipment to address the above issues. This and other early units were primarily lined with hard firebricks and backup insulating board materials. Other designers of FCCU's have been Universal Oil Products (UOP), MW Kellogg, Brown & Root, Foster Wheeler, Sterns-Roger, Stone & Webster and others.

During WW2, there was a shortage of skilled brick layers because of the war effort. With this shortage came to need to rethink the refractory lining design for such complex geometric designs. In the early 1950's calcium aluminate cements were in the early stages of development. Calcium aluminate cements were beginning to be combined with various aggregates such as calcined fireclays, bauxites, crushed insulating firebricks and lightweight aggregates like haydite, vermiculite and later vermiculite, were beginning to be used to make refractory concretes known as castables. Pneumatic guns used to transport these castable materials through reinforced rubber hoses, tempering them with water via a water valve, water ring combination at a nozzle that "shot" the wet concrete mixture against the metal casing being lined. Anchoring designed to hold the linings in place consisted of a variety of systems including wire mesh, chain link fence , or “steer horns”, and other types. Somewhere in the early history, it was found that what was often used to wipe dirty shoes on, hex shaped metal” was good as a lining anchor. This later became known as “hexmesh” or hex metal. The installation of refractory linings in process equipment was very specialized.

With increasing demand for gasoline in the USA, and gasoline being the primary fuel produced by the FCCU process, profitability was immediately demonstrated in the earliest units.

In the early years of FCCU operation, refractory lining installation companies began to spring up specializing in refractory installation and lining repair services to the oil refining industry. Many of these early contractors used equipment designed for the concrete industry to “field mix” the various refractory components of a castable in the field. One of the most common refractory castables used in fired heaters and in some FCCU equipment was the “LHV 1:2:4” castable. This refractory type involved mixing 1 volume part of Lumnite cement (a low purity calcium aluminate cement manufactured by Universal Atlas from blast furnace slag), 2 volume parts haydite, a diatomaceous earth light weight aggregate having a density of about 28 lb/ft^3 and 4 volume parts of vermiculite an expanded mica of about 5 lb/ft^3. LHV 1:2:4 continues to be listed on old drawings and in some furnace specifications.

It took much skill and experience with lining equipment and refractory materials in order to repair refractory linings inside these very complex units. Field mixed refractory and proprietary pre-mixed refractory products designed for casting were installed using any manner of refractory conveyance at that time. It was not unusual for a refractory lining material to require 100% or more of extra refractory beyond what was required considering the installed lining density and thickness. As an example, when lightweight refractory castables were installed by casting, the installed density might be 50 lb/ft^3, but when installed by gunning, might be 70 or 80 lb/ft^3. Given the increase in density and the loss in rebounds (refractory material not sticking to the gunned surface) the contractor could run out of the needed amount of refractory very quickly.

Unlike the oil and steel industries, that had a tendency to use very high volumes of refractories on a regularly scheduled basis. Tons of steel per ton of refractory was a measuring rod for performance of steel mills in the 70’s. There has never been a measure of gallons of gas per pound of refractory. The measure of success in the refining industry was the length unit run.

In the early 1950, FCCU’s would run 3 to 6 months before needing to be repaired. The faster the repair could be made and the unit placed back on line, the better. The scheduled shutdown was known as a Turn-Around. Although the industry has been profitable, it has been very competitive. Profits have often been measured in cents per gallon of product. Refractory installation contractors who understood this dynamic understood that the faster they could repair a lining and get the unit back up on line, the better.

In early days of the refining business, most refractory manufacturing companies were preoccupied primarily with servicing the high volume iron and steel industry. Paper and cement kilns were also good, high volume business for refractory manufacturers. Refractory installation contractors became the chief motivators to get refractory companies involved in designing refractory lining systems for the petroleum industry in the early years. Refractory Services Company, now Resco Products, Inc, in particular responded well to contractor pressure. Resco developed a line of refractories for the FCCU which installation contractors learned to depend upon. This refractories line included Rescobond AA-22, an air setting phosphate bonded erosion resistant refractory to resist erosion by fast moving catalyst in the catalyst separation and transport system. A second product that because a utility product in the industry was RS 17-E, a high cement calcined fireclay aggregate refractory was used in high erosion areas where both erosion resistance and heat insulation were required. RS 3 was a medium weight refractory designed for the main FCCU vessels were there was no significant concern about erosion, but where heat conservation would be needed.

Until the late 1960's and early 1970's basic designs in FCCU's consisted of the following:

- For highly erosive parts of equipment such as catalyst separation cyclones, slide valve discs and other internals where erosion resistance was required with no concern about thermal insulation, thin, ¾" or 1" linings anchored with hexmesh were used. In the early days, either 94% alumina or dense alumina-zirconia based castables or Resco Products AA-22S was used in this service.

  Extreme skill was required for the installation of each of these products. The castables needed to achieve a stickiness that would allow them to be packed into the hexmesh in vertical and overhead positions. In shop installations, this was not a concern since cyclone barrels could be turned and packed downhand, but it was very difficult when performing maintenance work when the cyclones were in place.

  AA-22 phosphate bonded refractory was an ambient temperature phosphate bonded refractory that was shipped in two components, a white dry component and wet component died red which contained a phosphoric acid. The white component had an air setting agent in it that, when mixed with the wet component and a small amount of water in a high speed mixer reacted with the phosphate to form a room temperature set. The product was known to be very sensitive to water addition and ambient temperature. It was not uncommon for a batch of mixed refractory to get up to 150 to 200°F during mixing and installation. The product would also harden or set up very quickly and often had to be discarded because it could not be intalled. The Hobart dough mixer was identified as the best mixer for mixing this product.

  AA-22 was to have a stiff putty consistency when mixed so that it could be pushed into each hex in a hexmesh anchored lining. Despite the difficulty in installing the product, in the 1970's AA-22 was the pace setter for erosion resistant linings in extremely erosive service. At that time, AA-22 had erosion resistance, when properly installed, of 8 cm^3. Refractory installation contractors who used high volumes of the product for shop and field installation work became wise in the installation tricks for optimizing AA-22 installation. Some chilled the product, chilled the water and installed the refractory in a cool room when performing shop installation. This provided time to optimize the installation uniformity and also resulted in the best possible erosion resistance. The practice of adding too much water during mixing was one way to get the refractory in place in the field, but resulted in sharply compromised physical properties.

The success of AA-22 in the 1970's stimulated companies to attempt to either duplicate it or offer improved alternative products. This was especially in light of the number of FCCU's that were being built in the 1970's and 1980's. One effort by at least two companies included the use of fine aggregate sized high alumina phosphate bonded plastic refractory. Because the phosphate bonded refractory did not contain an air setting agent, it was shipped in a putty consistency ready for installation. There was no major rush to install the refractory because of fast setting characteristics. The installers could pack the refractory in place, use Teflon blocks and pneumatic rammers to get the refractory packed well in and around the anchoring. Some of the phosphate bonded plastic products used in the 1980's for cyclone linings are still in service today. The issue that kept phosphate bonded plastics from gaining acceptance in field work was it doesn't gain strength until it is heated.

In the 1980's Resco products found a way to combine both the air setting agent and the phosphate bonding system in AA-22 into one component. The new product became known as AA-22S (the "S" signified single component.). The new product became easier to mix and install and ASTM C-704 erosion resistance was improved from 8 cm^3 down to 6 cm^3 loss. Installation became easier and the range of water addition required to reach the advertised erosion resistance was widened. In the 1980's and most of the 1990's AA-22S was the primary product. Product improvement increased to the point that in the late 1990's the product was able to be installed at erosion loss numbers consistently less than 4 cm^3.

In the 1990's a new product was invented that had a relatively long working time and erosion resistance values consistently less than 3 cm^3. Actchem 85 was developed in South Africa and became a significant competitor to AA-22S in the late 1990's and 2000's in the USA. Other products have been designed around the idea of these two product and erosion resistance. Some products are available that now have erosion resistances at about 2 cm^3.

- One essential item in FCCU's is what is known as catalyst transfer lines and flue gas lines. The catalyst transfer line's sole purpose is to circulate catalyst from one vessel to the next or to the point where the catalyst will be contacted by the feed for the cracking operation. Although not as erosive as transfer lines, flue gas lines off regenerators are refractory lined and vapor lines off reactor vessels are often refractory lined. The purposes of the linings in these lines is both erosion resistance and thermal insulation in the case of cold wall lines (less than 650°F metal shell temperatures) lines, and erosion resistance in hot wall lines (greater than 650°F metal shell temperature).

  In the 1950's through 1970's, both erosion resistance and thermal insulating capabilities were achieved through a dual layer lining system. This lining system consisted of a 3 or 4" insulating (50 to70 lb/ft^3 backup lining with about 2" high circumferential ring vapor stops seal welded to the metal shell to minimize the possibility of gas and catalyst erosion of the metal casing. The hot face lining was anchored with hexmesh welded to 2” X 2” square headed “T” studs and packed with an extreme erosion resistant refractory. Problems that developed in these linings were related to weld failure between hexmesh and the “T” studs. The hexmesh expanded at greater rates than the “T” studs that were welded to the metal shell causing rips and openings in the hexmesh. This allowed catalyst and hot gases to bypassing behind the erosion resistant lining and eventually erode out the backup lining leading to hot spots and possible hole throughs in the line.

In the late 1970’s based on the poor performance of this design, the strategy became to begin to use high calcium aluminate cement containing fireclay castables in cold wall catalyst transfer, flue gas, and vapor lines. A number of generic fireclay castables were available for this use as supplied by several suppliers. Exxon Research & Engineering labeled these types of products as “erosion resistant heat insulating”.

A problem identified in the industry concerning these products in the early 1980’s was that although most had about the same densities, chemistries, and strengths, the published coefficients of thermal conductivity or “K-factor” for them ranged from less than 5 BTU/hr/ft^2/°F/in. to about 8.5 BTU/hr/ft^2/°F/in. when test at 1000°F. This difference in “K-factor” can make a significant difference in metal shell temperatures. When operating transfer lines and 80°F ambient temperature and 0 mph wind velocity, the metal shell temperature of a 5” thick lined pipe will be either 332°F or 410°F depending on which K-factor is correct when the process temperature is 1225°F. Metal shell temperatures would be either 358°F or 450°F for 1400°F process temperature for the same lining thickness. From experience, it was found that the higher K-factor was closer to the right value. Some units were being designed using the lower K-factor.

To address this issue in the early to middle 1980’s:

- More stringent testing requirements were placed on thermal conductivity;
- An evaluation of the ASTM C-417 calorimetric method indicated that a quicker, and less variable dependent test procedure was needed;
- The JIS R-2616 hot wire method was found to provide quick values that were about 20% higher than those generated by ASTM C-417;
- ASTM C-1119, very similar to the Japanese hot wire tester started being used on a regular basis.
- Refractories companies begin more carefully measuring K-factors;
- Exxon Research & Engineering designated a new category of refractory which would have density less than 120 lb/ft^3, erosion resistance less than 20 cm^3, (the original heat insulating erosion resistant values as required per BP 19-3-2 of less than 14 cm^3) and a K-factor of less than 6 BTU/hr/ft^2/°F/in (the originally required value was 5.5 BTU/hr/ft^2/°F/in).

This new refractory type was designed to be used for flue gas and vapor lines which were much less erosive than the transfer lines. The medium weight heat insulating fireclay castables continued to be used in transfer lines because of the concern about erosion resistance. From these new requirements came new products nearly complying with those shown above.

The first use of vitreous and fused silica castables introduced based on these new requirements. With this first use came the thought that the very low coefficient of thermal expansion for fused silica may make it more reliable in some of the thermal shock application such as feed risers where warm oil, hot catalyst and steam or mixed in the cracking operation. There some reported success in this service. The drawback concerning the use of fused silica to meet the flue gas line refractory service is that the coefficient of thermal conductivity for the amorphous silica is high relative to that even of fireclay castables.

With competition high, new products began to flow. These high cement, haydite based products had densities of 110 to 120 lb/ft^3. Two or three new products developed in this time frame had densities, strengths and erosion resistances within the range acceptable for transfer line use. One product in particular was installed in a regenerated catalyst transfer line in the 1990's and continues to perform satisfactorily in that service. When installed with special care, one product has consistently demonstrated erosion resistance less than 10 cm^3 and a K-factor between 6.2 and 6.7 $BTU/hr/ft^2/°F/in$ at 1000°F when tested by the ASTM C-1119 hot wire method.

Even prior to new product development, refractory installation contractors were quickly developing installation methods designed to enhance installed refractory lining quality. Until the mid 1970's most of the linings in transfer and flue gas lines were installed by hand packing, or gunning. With the new heat insulating erosion resistant linings, equipment designers began to specify that these linings be installed by vibration casting rather than gunning or hand packing. As far as is known, the first transfer line was installed by casting with the pipe laying down horizontally and casting 120° segments of the lining, allowing to air cure, and then turning and casting until the full lining had been installed. Although the lining uniformity was good, the key issue with such and installation procedure was the longitudinal joints that would permit catalyst and hot gas bypassing along the cold joint to the shell.

To address this, Hi-Tech refractories in Houston built a tower designed to enable sections of piping to be stood up vertically and cast so joints would be circumferential and not longitudinal. They would attach high power vibrators to the metal shell by chains and come-alongs at various heights up the pipe and cast medium weight castables at minimum water content using high vibration.

Another innovation in these lines in the 1970's was the addition of nominally 1" metal fiber reinforcement into the mix intended to enhance the tensile strength and to evenly distribute shrinkage cracks in the lining. Initially, metal fibers were drawn wire fibers. As the demand increased, moon shape sectioned melt extract fibers and sheet chopped fiber have also been introduced. Drawn wire fibers can be used in cast installations, but tend to stick in rubber material hoses for gunning resulting in plugged equipment.

- The third type of refractory that has seen considerable use as linings in cold shell FCCU regenerators and reactors is the medium weight heat insulating castable and gun mix. When brick linings were replaced in FCCU regenerators and reactors, the medium weight refractory began to be used. The product was installed by gunning. This became a very big market for a number of refractory suppliers in the 1970s through the 1990's when a number of new FCCU's were being built. The gunned installation was the fastest installation technique.

  In the 1970's installation contractors began pressuring refractory suppliers to redesign this type of refractory castable for installation by gunning. In response, a number of new products with the designation "G" for gun mix or gunning after the product name were designed for this installation. Some of the development work also included fine tuning the types of gunning equipment that would result in the best refractory linings. A good gunning mix refractory should have reproducible as-installed physical properties, have a wide nozzle water addition range for ease of installation with minimal dusting and no slumping on reaching the target wall.

  With this work, refractory materials became far more installer friendly, and the quantities of refractories needed for an installation and the speed of the installation were improved. The installation was also very dependent on the quantities of water added to the refractory prior to charging it into the gunning equipment, having adequate air pressures, proper feed motor to feed wheel ratios, and properly designed feed wheels. The type of gunning equipment was also essential in ensuring a good refractory installation. The designs of pneumatic guns available over the years have included the Jetcreter (rotary) gun, the Boulder (dual chamber feed) gun, the Allentown (dual chamber feed) gun, and the Reed (open hopper, rotary feed bowl) gun. Experience normally indicated that the dual chamber feed guns, when operated with a properly designed accessories and a skilled gun operator will provide the smoothest flow of refractory through the gunning equipment.

  Factors that affect lining quality at the nozzle include adequate water pressure to the water ring in the nozzle assembly, a properly sized water ring located at a distance far enough back from the nozzle to provide good mixing of the refractory and the water prior to flowing out of the nozzle, a needle valve on the water line to provide careful control of the amount of water being added at any one point in time, an appropriate nozzle that allows the nozzleman to have good control of the mixed refractory flow, and a skilled nozzleman having good experience in handling both the nozzle assembly and the refractory being installed.

  With all the skill and care of the gunned installation, there are inherent shortcomings in refractory linings that are installed by gunning. These are the laminations that, although not always identified by hammer test or in nozzleman qualification testing, which form and are approximately parallel to hot face surfaces. When rebounds (refractory not sticking to the gunned surface during installation) occur for medium weight refractory material, the rebounds are normally the insulating aggregate that provides the thermal insulation capabilities of the refractories. With these two issues and the amount of catalyst that filters into lining imperfections for FCCU regenerators, there is a tendency with thermal cycling for the lining to spall or lose sheets of refractory from the hot face of the refractory lining.

On refiner reported excessive gunned lining repairs in the regenerator at each Turnaround. In an effort to solve this problem, they installed what is believed to be the first pump cast medium weight lining in an FCCU regenerator during the first part of the 1990's. As of the end of the late 2000's the pump cast lining has yet to require repair. At this point, the lining has been in service for well over 20 years.

While considering the pump cast installation of a refractory lining in a regenerator several years ago, a phone conversation with the contractor who performed the above pump cast operation somewhat discouraged the installation method. Simply put, the contractor had lost a tremendous amount of repair work because of this installation.

Pump casting installations have continued to increase. In 2011, aside from top head linings, a major FCCU with three major vessels and all of the transfer and flue gas lines installed by either the pumpcast or the vibration cast method. What was seemed impossible as few as 20 years has been accomplished in recent years.

As mentioned earlier, many of the refining companies depended heavily on the installation contractors for advice concerning which refractories were to be used and how they were to be installed. But in the 1960's and 1970's refractory use in refineries was becoming so important that oil companies began hiring ceramic engineers to oversee refractories technology for their equipment. Four of the first engineers primarily responsible for refractories in the oil companies were Dr. Mike Crowley of Amoco, Charles Venable of Phillips, Don Becker of Conoco and Ray Searles of Mobil. Mechanical engineers such as Ed Shoemocker and Stan Bronson of Exxon Research & Engineering and others were charged with following and developing the refractories technology. In the 1970 and 1980's the numbers of ceramic engineers in the refining industry has increased dramatically. In Exxon Mobil Research & Engineering alone, the number of ceramic engineers following licensee and affiliate work is four and was as high as six in the early 1980's when synthetic fuels development was ramping up and before the precipitous drop in the industry.

In the early years of refractories for FCCU's, products were selected for use based primarily on brand name recognition. "If Brand X was installed in the past, then Brand X will be the product used again." No efforts were made to identify just why one product worked better than the other. That began to change in the late 1970's when Exxon Research & Engineering Company prepared a basic practice for fluidized bed equipment and stated the physical properties they were expecting to achieve in the actual installation. Admittedly, at that point in time, there were only certain refractory materials that would accomplish what was specified, but the listing of physical properties requirements challenged serious contenders to the mainstays. This was very good for the refractories industry.

In the early to middle 1980s, another factor was added to enhance installed refractories in FCCU's and other pieces of process equipment. This was the introduction of the first inspection and testing company dedicated to QC and QA for refractories primarily for the refining and petrochemicals industry. Robert J. Jenkins started the R. J. Jenkins Inspection Company at that time. With the opportunity to use a third party inspection group who also tested pre-qualification and as-installed samples, this complimented the establishment of physical properties requirements for refractories to be used in the refining industry. Since the establishment of the Jenkins inspection company and testing laboratory, several other inspection companies have been established to perform testing.

In the early 1990s, in the absence of industry testing standards, the American Petroleum Institute formed a task force with the charter to establish a sound testing protocol to be used for confirming quality of refractory linings primarily used in fluid solids equipment such as FCCU's and fluid cokers. John R. Peterson of ExxonMobil Research & Engineering was elected to chair the task force in an effort to complete this charter. The first draft of API Recommended Practice 936 was approved for use in 1994. Since that time, there have been three revisions to the document which is now API **Standard** 936. During the 20 years of meeting twice a year, many relevant topics have been debated and address in the task force meeting. Those in attendance over the years have been refractory suppliers, installation contractors, refractory testing companies, refinery equipment designers and end users.

Some very significant work the Task Force has performed concerns the fine tuning of ASTM test procedures considered critical to FCCU refractories. One in particular has been the ASTM C-704 test. Some of the users of this procedure are not as concerned with the precision required when developing the most erosion resistant refractors and testing them at a number of different locations. With the replacement of the sand blast gun with a machined block to reduce test variation and the introduction of an internal glass plate standard, the reproducibility of test erosion test results will be sharply improved. This is just one example of the work performed in the task group.

For the past three years, the API Refractory Task Force has been working on a refractory supplement to be used in combination with the API Standard 560 for fired heaters as requested by the API 560 committee.

Another group of refractory practitioners has recently been working diligently on a set of Process Industry Practices (P.I.P.s) to provide good practice information for the application and use of refractory in process equipment. When completed these PIPs will be very helpful documents for use in refining and petrochemical applications.

Lining reliability in FCCU's has sharply improved since the early 1950's when a very good period of unit operation was 18 months. The time between shutdowns has sharply improved in recent years. At one point, 3 years was considered very good. Some refineries have operated their FCCU's as long as 6 or 7 years without the need of significant maintenance. So from 18 months, to 6 years is quite an accomplishment.

Another are that has required significant work in recent years has been sulfur recovery equipment and incinerators. The United States holds the highest standards for pollution control equipment in the world for petroleum oil refiners and petrochemicals producers. A key piece of high temperature equipment used to remove sulfur from the process gases is the sulfur recover unit (SRU).

Sulfur from acid gas is the Claus unit. The first of these units was commissioned in the 1950's in Canada and is now in wide spread use in the United States. Depending on the amount of acid gas being converted to from H_2S and O_2 eventually to S and H_2O by both thermal and catalytic reactions, temperatures in thermal reactors can range from 1600°F to as high as 2800°F when properly designed.

With the need to control emissions and with the amounts of sulfur being processed out of heavy sour (sulfur containing) crudes, efforts have been made to increase throughputs for these units. Oxygen enrichment is the current method used to upgrade the unit so that more acid gasses can be processed through the unit. A key issue related to the O_2 enrichment has been the inability to monitor thermal reactor temperatures. When the stream of acid gases is reduced, there needs to be a corresponding reduction of O_2 in the equipment since the success of this process upgrade depends on having sufficient feed to absorb the high heat afforded by the O_2 enrichment process. When temperature measuring devices have not been working properly, temperatures in thermal reactors have been known to go as high as 3100 to 3200°F. If this happens, the refractory lining life will be sharply reduced and there may be a rupture of the tubes in the boiler attached to reaction furnace.

In the earlier process designs, refractory lining systems were not as critical as they are today. It is normal for a refinery to have two and possibly three SRU trains in case of the need to perform a repair on one of the units. If a refinery were to have only one SRU, if that unit should experience operational problems, the entire refinery would need to be shut down until the repair could be completed.

In early SRU thermal reactors, bauxite based refractories have been used. These linings have become obsolete with the higher temperatures being achieved with O_2 enrichment. The standard refractory lining design used today in reaction furnace is 6" of a mullite bonded 90% Al_2O_3 brick backed up with 4-½" of 2800°F insulating firebricks.

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