In preceding sections of this report, there have been a number of references to materials problems and the modifications to process or component designs which have been reported to alleviate the problems. Here we will attempt to summarize available foreign materials experience on the basis of unit operations within a typical coal liquefaction plant.

## 4.1 Gasification

Although a separate assessment of gasifiers was prepared by others,[14] they are included in this report on materials for coal liquefaction because a gasifier is necessary in all liquefaction processes either as a starting point for indirect liquefaction or as a source of hydrogen for direct liquefaction. Considerable information on materials problems and some resolutions have been reported for various gasifiers. In the following discussion of the gasification process area the available information from various foreign activities is grouped into similar functional components.

Two types of gasifiers have the most operational experience. These are the Lurgi fixed-bed dry-ash gasifier and the Koppers-Totzek entrained-flow slagging gasifier. The Lurgi utilizes a water-cooled carbon steel jacket without a refractory liner. No significant problems with the jacket have been reported. The Koppers-Totzek (KT) also has a water-cooled jacket but is dependent on a refractory liner that in large part is composed of frozen slag. At Modderfontein in the Republic of South Africa, synthesis gas is produced by AECI Ltd., utilizing KT gasifiers. During early operation in 1975 the 40 mm (1.5 in) refractory lining was seriously attacked by slag in the first few months of operation.[15] This was attributed to the fluidity of the slag at the relatively high operating temperatures required by the low reactivity of South African coal char. The initial fix was to lower operating temperatures by decreasing the $O_2$/coal ratio. This protected the refractory, but adversely affected conversion efficiency. Subsequently, the gasifier wall was modified by increasing the number of studs anchoring the refractory to the water-cooled outer wall. The effective thermal conductivity of the composite wall was raised sufficiently to insure a protective frozen slag layer on the refractory, even at efficient levels of operating temperature. Further studies of the characteristics and properties of alternative coals originated with this problem. This points out the significance of the coal source in defining process and materials choices. Coal from the same seam but with different ash composition was found to permit a 150°F higher temperature operation and improved efficiency.

The Shell-Koppers (S-K) gasifier under development in the Netherlands and the Federal Republic of Germany is a pressurized modification of the K-T gasifier. Reportedly,[16] the refractory is not a problem even though a range of coals has been gasified in the pilot plant at the Harburg Refinery where the pilot plant is located. In the combustion zone the pressure vessel has an internal water wall covered by refractory; with time the refractory is replaced by frozen slag. The upper quench zone is a refractory-lined hot wall design and at <900°C (1650°F) presents no problems. A hot-wall combustion zone tested at Amsterdam has presented unsolved refractory problems. With a properly designed water wall, the only refractory problem would result from burner misalignment after maintenance. This occurred at Amsterdam, was recognized from the resulting hot spot, and was readily corrected during operation with the frozen slag wall being fully restored.

Typical of a hot-wall gasifier is the Texaco gasifier. With this approach additional stress is applied to the refractory liners, and a number of sites have reported refractory problems. In particular, various applications of Texaco gasifiers seem troubled by refractory degradation. At the demonstration plant of Rhurchemie/Ruhrkohle at Oberhausen-Holten initial refractory gasifier liners had to be replaced after only about 1500 hours.[17] The Ruhrkohle staff feels that two- to three-year lifetimes are required for economic commercial operation. Special attention is being given to the corroding and/or eroding attack of the liquid slag on the reactor lining. This may be controlled either by non-cooled refractory linings of special composition or by water-cooled metallic walls. In special test zones incorporated in the lining of the reactor jacket they tested some fifty different refractory materials from various manufacturers. In the initial period this procedure led to inferior lifetimes of the reactor lining, since the stability and the resistance of the whole lining were determined by its weakest constituents. During the first year of experimental work, however, so much information was obtained about suitable and unsuitable materials that a reliable choice of qualified ceramic lining was possible. To this end lifetimes of 5000 hours and more are now expected, and this despite extensive pilot plant work with its frequent change of reaction conditions. This lifetime is expected to be extended considerably during proper and constant operation.[18] Despite this improvement in refractory life it has been reported that Ruhrkohle is working on a water-wall modification independently.[16,17] The BASF ammonia plant in Ludwigshafen also uses a Texaco oil gasifier to generate synthesis gas. They, too, have had problems of cracking and crumbling of the alumina refractory brickwork adjacent to the burner entry point.[19] These problems seem to have been corrected by modifying the wall contour and controlling the ash-forming components in the recycle feedstock.

Coal feeding systems for most of the gasifiers are currently dry systems utilizing lock hoppers with or without screw feeders and blow pipes. Very little materials information was found for these areas. In general it appears that carbon steel and low alloy steels are generally used with hard facing of some components to improve wear resistance. Since the feeding and control of the burners is a critical proprietary area very little detailed information is made available. At the Saarberg-Otto gasifier, dry coal screw feeders were replaced with gas transport jet feeders.[17] At the Sasol One facility,[20] coal is carried to each Lurgi gasifier unit by bucket conveyor; each unit has two bucket conveyor systems: a primary and a spare. The redundancy implies vulnerability. Feed hoppers require annual repair. But these components operate at near ambient temperature. Erosion in the blow-pipes for the Modderfontein KT gasifier has been reported [20] to require these components to be replaced on six-month intervals. Perhaps as a result of this experience or some erosion of the burner heads,[16] the Shell-Koppers pressurized modification of this gasifier includes features for on-stream replacement of burners.

At the other end of the gasifiers, problems with the removal of ash and slag have been reported. At Sasol the ash removal system, including the ash grate and ash lock hoppers, is subject to high temperature erosion of moving parts. This damage is repaired on a three-month cycle which determines the facility maintenance schedule. It also requires the operation of 13 gasifier units (and their ancillaries) to keep 11 on line all the time, implying an approximately 20% penalty in capital costs attributable to high temperature erosion. Improvement of the ash grate and ash lock hopper systems to achieve lifetimes greater than three months has the highest priority in the continuing Sasol One equipment development program. After depressurizing the ash is sluiced away. There have been no really successful attempts to pump the ash away. Erosion of the pump impellers and steel pipes is significant.[21] On the other hand, the Ruhrchemie/Ruhrkohle group has reported little trouble with their slag removal system for a Texaco gasifier.[22] Here, removal of the coarse ash includes wet granulation in the pressurized hopper. Specialized valve types that are also suitable for highly abrasive solid matter are installed in a programmable lock system so that they are not subject to erosion attack from the flowing ash suspension. "The discharge system for removing the slag from the pressure body does not present problems any longer. Difficulties which arose initially due to the unexpectedly low bulk weight of the slag, resulting in a low sinking speed in the water phase and very high transport volumes, were eliminated by design changes. The electronic control of the lock system has worked since then completely without problems and without manual adjustment. Basic erosion problems on the discharge components did not develop. Reportedly,[16] a similar system of grinding the water-quenched slag, for the Shell-Koppers gasifier at the Harburg Pilot Plant, before pressure let down though a lock hopper system has worked very well.

While carbon steel appears to be the predominant material choice the corrosion rates have not been discussed for the slag receiving and slag removal equipment. Increasing utilization of recycle water systems may cause problems in this area in materials choices. This has already been noted in the Ludwigshaven Texaco oil gasifier. Water in the bottom of the reactor is used to quench the generator gas and remove unreacted carbon in the form of soot. As drained from the reactor, the sooty water also contains 0.1—0.15% formic acid. The acid caused extensive pipe corrosion between the reactor and the soot separation stage where the water, after scrubbing with naphtha, is decanted. Attempts to neutralize the acid with ammonia would have eliminated the corrosion, but also caused emulsification, impeding the separation of water and naphtha in the decanter. The vulnerable piping was replaced with "alloyed steel pipe" which has apparently resisted corrosion successfully.[19]

Waste heat recovery is an important part of the gasifier processes. Erosion, corrosion and fouling have all been reported as problems for various gasifiers. Erosion, which has been related to the coal ash characteristics, has been a problem with the Koppers-Totzek gasifiers at the Modderfontein Plant. In this design of these gasifiers the product gas is quenched as it leaves the reactor and is conducted vertically upwards through a tangent tube boiler. At the top of this boiler the gas stream is split, each portion making a 90° turn through the two arms of a tee (also constructed as tangent tube boilers). After a short distance both streams are redirected downward at a 45° angle through the tubes of a final boiler in which steam is raised in the shell. It is at the point where the gas must make sharp 90° turns that severe erosion problems have been experienced and it is thus this section of the gasifier that appears to limit reactor performance by creating a requirement for frequent maintenance. The velocity of the gas stream in the heat recovery section generally makes it unnecessary to employ soot blowing to keep tubes clean; however, the resulting erosion is so extensive that the use of refractory shields at sharp turns in the duct work has been only partially successful at coping with the problem. At present, silicon carbide tiles are used to shield prime erosion areas; yet even this extremely hard material will last only 3-6 weeks before maintenance is required.[20]

In addition the tubes in the tangent tube boilers in the vertical riser and tee cross legs have been eroded at rates up to 4.75 mm (0.2 in) per 1000 hours. Since the erosion is localized it has been arrested by installing protecting plate made of type 310 stainless steel. Abrasion resistant alumina coatings are also being tested.[23] In heat recovery systems with lower gas velocities corrosion and/or fouling have been reported as problems. At the Shell-Koppers pilot plant in Amsterdam, corrosion cracking attributed to chlorine led to the replacement of Incoloy 800 with Incoloy 850 for the waste heat boiler tubes. Fouling of the waste heat boilers has also been reported for a number of gasifiers. The Texaco gasifier demonstration plant at Oberhausen initially experienced[17] problems with deposits in the waste heat boiler due to molten ash carryover. However, it has been reported[16] that since modifications were made to the waste heat boilers there have been no fouling problems. While fouling, per se, is an operational rather than a materials problem it does affect the frequency and intensity of soot blowing. At the Koppers-Totzek plant at Talcher, India[24] erosion from soot blowing operations was found on the economizer and evaporator coils of the waste heat boiler. Although the erosion was apparently eliminated by reducing the soot blowing steam pressure, this remedy may not be effective for deposits with different ash compositions.

In the process area of raw gas cleanup and quenching very little materials information has been found in the literature. A variety of systems employing centrifugation followed by water washing or multiple washing stages are used in various pilot and demonstration plants to remove oils, tars and flyash. Both erosion and corrosion can be anticipated in these systems. The need to protect downstream equipment and subsequent processes has been emphasized by all developers. In most cases the scrubbed gases must be recompressed before entering the subsequent processes; thus, compressors and interstage coolers are considered here as parts of the raw gas pretreatment area. Operational problems with solids deposits in the compressor area have been reported for Koppers-Totzek gasifiers in two locations: Modderfontein[25] and the Nitrogenous Fertilizer Industry SA in Ptolemeis, Greece.[26] Fouling of the off-gas washer-cooler due to fines carryover was also reported for the Grecian installation requiring a short shut down of each of five gasifiers every four to five days. No real information on corrosion in this process area was defined. However, problems with corrosion if the feed materials contain significant chlorine can be inferred from the experience at the Ludwigshafen plant[19] referred to earlier in discussing slag removal and in some of the subsequent processing steps in the following discussion.

For gasifiers in a direct coal liquefaction process the objective is to produce the required hydrogen. The raw gas is generally shifted to maximize hydrogen production and the acid gases $H_2S$ and $CO_2$ removed. The order of processing varies in existing gasifier installations depending on the plant product requirements and process design. At Modderfontein the shift conversion occurs after a Rectisol treatment to remove the $H_2S$ and COS from the gas. In the shift conversion subsystem, pressurized recycle water is contacted with a gas containing a high partial pressure of $CO_2$. This produces carbonic acid at high temperatures up to 240°C (460°F). The corrosiveness of this acid was compounded by erosion attributed to relatively large amounts of catalyst dust suspended in the water. This aggressive medium led to severe corrosion/erosion of carbon steel water heater tubes and saturator and desaturator distribution trays during the first two years of plant operation.[25] The initial fix was substitution of stainless steel for carbon steel in the regions of most severe attack. Subsequently, it was found that the corrosion/erosion rate is dependent on the fluid turbulence and the pH. Therefore, limitations on maximum allowable liquid velocity have been instituted. The velocities allowed are much lower than those conventionally used, as low as 2 m/s (7 fps) depending on pH. At the Ludwigshafen Texaco oil gasifier[19] the importance of removing chlorine in the gas washing operations has been identified. Here a sour shift process is used. High pressure and the presence of $H_2S$ required "extensive use" of "alloyed steels" in the CO shift conversion unit. However, stress corrosion cracking (SCC) was found after several months of operation. The chloride activator of the SCC was traced back to the approximately 50 ppm chlorine in the fuel oil being gassified. Chloride film sediment was deposited in the shift convertor pipes by condensation of water containing trace chlorides during shutdown procedures and subsequent evaporation of the water during startup. Repetition of this cycle resulted in the buildup of deposited chloride level to concentrations effective in causing SCC. Elimination of chloride stress corrosion cracking was approached both by limiting the opportunities for chloride deposition and by using materials less susceptible to SCC. Provisions have been made to drain condensate after a shutdown, before it can evaporate. And "extensive use has been made of both ferritic and austenitic materials" which are stress-relieved at all welds. In this same plant cracking of the water-cooled oil burner was attributed to a combination of $H_2S$ corrosion and thermal shock. Substitution of an iron-chromium-nickel alloy has mitigated the problem. Burners have to be replaced at four- to six-week intervals because of burn-up of the oxygen nozzles. Tests on a new configuration using a more oxidation-resistant material seem to indicate the potential for improved performance.[19]

## 4.2 Liquefaction

In the literature, trip reports and discussions with foreign visitors there has been even less materials information divulged about liquefaction than that available for gasifiers.

### 4.2.1 Valves and Pumps — A Generic Problem

The most serious difficulties seem to be encountered in ash handling equipment, and in components controlling solid/fluid mixtures flow. Lock hopper valves and letdown valves are frequently mentioned[20,16,27,24] as critical components. For the lock hopper valves not all of the news is bad. Ruhrkohle reported[5] no problems with their ash lock hopper "because of good design and good material selection." Other reports of satisfactory component performance exist in the literature cited, but have not been highlighted here because of a lack of information or materials selection and design details. For pressure letdown valves there is very little materials information. That there are problems is evident. One response to this is the development by Saarbergwerke AG of an "expansion machine"[17] to replace all ash slurry letdown valves. The new device removes pressurized slurry with a piston-type device in conjunction with a series of programmed valves to eliminate high velocities and, thereby, reduce erosion rates.

This category of problem has also impacted devices that represent more of a departure from established coal conversion technologies. A nuclear-heated gasifier pilot plant[28] required modification of valves for gases containing dust as well as components of the ash removal system, helium loop, and fluidized bed. And in Japan, Hitachi, which is developing a direct liquefaction process, has reported[29] erosion problems in shaft seals and valve components. Replacement of tungsten carbide plates and seals on control valves with a Stellite material has produced superior performance; 37,000 valve cycles are said to have resulted in very little wear. Also a 20-fold decrease in slurry feed pump shaft wear was obtained by "external flushing". Slurry pumps are highly vulnerable and controversial components. Sasol recommends avoiding the use of slurry pumps altogether if at all possible. Their compatriots at AECI had the steel impeller of a high speed slurry pump wear out in less than a month. The single pump was replaced by a series of three rubber-lined centrifugal pumps and no erosion problems have been noted since.[20] These references dealt with aqueous slurry of ash from the gasifiers. Slurry pumps feeding coal process oil mixtures to liquefaction processes have high wear-resistance demands put on them because of the temperatures and high pressures. Significant development in this area is underway at the Bottrop plant of Ruhrkohle AG and Veba Oel AG in the Federal Republic of Germany scheduled to start up in July 1981.[30,31] Three slurry feed pumps were installed in the pilot plant, two operating, one spare. All three pumps are driven by SCR controlled electric motors. These pumps have three pistons working in parallel. For test purposes two of these pumps will work with the pistons in a vertical position; the third pump will have the pistons in a horizontal position. Remote valve boxes are connected to the pump via columns of clean oil. Due to the pump action some of the oil is lost in the valve box. This lost volume of oil is replaced after each stroke with clean oil. Through the design of the pump with an external valve box an abrasion free action of the pump piston is expected. In the valve box there are inlet and outlet valves of different design and materials in order to investigate their performance in regard to corrosion and erosion. No information is available on the materials being tested.

### 4.2.2 Slurry Preheating

At Bottrop they will also be testing slurry feed preheaters. Initial heating will utilize a feed/product exchanger but two types of secondary fired heaters, each with sufficient capacity for the plant operation, will provide the final heating. One second stage preheater is very similar to the ones used for hydrogenation of coal in Germany until 1945. In this type of preheater the heat transfer is achieved by circulating hot air through the shell and the slurry through the tubes. The heat transfer in this heater is very gradual and will prevent the slurry from coking in the tubes. The disadvantages of this heater are its size and the high cost.

The alternate preheater design installed has a radiation furnace of a type frequently used in oil refineries. Because of the higher temperatures the risk of coking is also greater. Minimizing this risk while utilizing the better heat transfer characteristics of a radiation furnace, its smaller size and its lower cost is the aim of this equipment evaluation test. Again no materials information was found, but this testing should be monitored. Other concepts in slurry preheating and mixing have been presented by Saarbergwerke AG.[32] Development in this area is to be done in the 6 T/d pilot plant they planned for startup in July 1981. No materials data are available but the concepts are worth continued surveillance especially since some materials requirements appear to be significant.

### 4.2.3 Pressure Vessels

The heart of the direct liquefaction processes is the reactor in which liquefaction of the coal goes to completion. These are typically large pressure vessels operating at relatively high temperatures (800–900°F). The operating pressures typically vary from 2500 psi to as high as 4500 psi in current processes. Early German processes were operated at pressures as high as 700 bar (>10,000 psi). The reaction phase may be accomplished in single vessels or a series of vessels depending on process conditions and designers choices. Materials properties and fabrication and shipping limitations have a large influence on these choices. The reactors are subject to creep, fatigue, and hydrogen attack at the temperatures and pressures of operation. Typically, the reactor vessels and other downstream high-temperature high-pressure process vessels are made of chromium-molybdenum alloys utilized in the petroleum industry to resist property degradation due to hydrogen attack. While there is a large diversified international development effort[33] to improve existing alloys and develop alternatives for these pressure vessel materials this development activity is not directed explicitly to the needs of coal liquefaction and therefore is not discussed here. Typically these large diameter high volume reactors are made from heavy wall materials such as forgings or plates. Fabrication processes are closely controlled and expensive. In operation, start up and shut down requirements are stringent and thermal cycle limitations may control the safe life of the vessels. Materials properties are dependent on heat treatment. Since practical heat treating processes as well as forming equipment capabilities limit wall thicknesses, monolayer wall vessel sizes are restricted to varying degrees depending on the process design operating temperatures and pressures. Thus indirectly pressure vessel construction and materials limit the options for the direct coal liquefaction processes. With this in mind the reactors being used in the pilot plant at Bottrop and the designs under development are of real interest.[31]

The reactors used in the pilot plant in Bottrop are of a new multi-layer design. These multi-layer reactors are of the cool wall variety for cost-saving. The internal insulation is retained towards the reactor cavity by a thin stainless steel liner which also protects the refractory bricks from abrasion by the slurry. During operation, the gases, specifically hydrogen, will penetrate from the interior of the reactor behind the metal retaining wall into the insulation layer and fill any empty spaces at operational pressure. In order to ensure unhindered refluxing of the gas into the reactor cavity in cases of dropping pressure, pressure relief apertures were provided in the metal wall. With gradual destressing of the system, pressure balance towards the insulation layer is maintained. In cases of abrupt destressing, a pressure buildup in the insulation layer may occur, leading to a mechanical deformation, viz. bulging, of the metal liner into the reactor cavity. Depending on the degree of deformation, the internal insulation may come off so that the reactor wall exposed to operational pressure is no longer heat-insulated. In this case, to avoid local overheating of the reactor wall exposed to operational pressure upon restarting, the internal heat insulation including the metal retaining wall must be replaced. A similar but novel reactor type is under development; it will no longer have the present drawbacks implied with pressure operations, specifically pressure drops, thus promising high availability and service life. The essential component of this development is a pressure-resisting metal retaining wall in between the internal insulation and the reactor cavity. The new reactor type is scheduled for installation and testing also at Bottrop. When testing is complete, the reactor will be removed from the plant and cut up for testing.

The reactor effluent is routed through a series of separator vessels to recover the excess hydrogen for recycle and separate the resulting oils from the ash and into categories for reuse as process solvent or further treatment. The initial phase separation usually takes place at high temperature and pressure in a hot separator where gas and vapors are removed from the top while liquid products and solids are discharged from the bottom. From the materials point of view this is essentially an appendage to the reactor with similar materials requirements. However, the much smaller volume and dimensions make fabrication much easier. Subsequently the stream containing the gases and vapors are treated at pressure but with cooling to condense the vapors followed by gas scrubbing to purify the recycle hydrogen. Materials problems with corrosion from $NH_4Cl$, $H_2S$ and sour water are anticipated but no specific problems or materials solutions were identified from the foreign sources during this assessment.

The oil liquid-solids slurry from the hot separator is treated typically by pressure reduction together with some temperature reductions. Both erosion and erosion/corrosion affect equipment design and materials choices in this functional area. The problems with pressure let down devices were discussed earlier in terms of valves and pumps but unfortunately essentially no details are available.

Erosion and erosion/corrosion where there are solids suspended in the liquids has long been recognized as a materials selection problem for both gasifiers and liquefaction plants. In addition, the corrosive action of sulfur particularly in conjunction with chlorine in the overhead stream from the hot separators has been noted for liquefaction plants.[34,35]

We have previously noted a materials choice concern with the presence of chlorine in the coals to be liquified. Early German work found that chlorine was a necessary ingredient in the slurry fed to the liquefaction reactors but led to materials corrosion problems in subsequent process equipment. The following excerpts from the book Catalytic Hydrogenation of Coal Tar and Oil Under Pressure by Dr. W. Kronig[34] highlights some of this experience.

> "The favorable catalytic action of the combination of tin and chlorine which had been determined in small scale experiments was confirmed in the commercial plants. The results in these plants were satisfactory in a chemical sense and the expected annual production of gasoline was reached.
>
> However, the catalyst, chlorine, has the disadvantage that it is very corrosive in certain temperature ranges. This has been found to be the case in small scale experiments after only a few operating days in the cooling zone of the products that left the hot catch pot. Corrosion began at about 410°C and ended at about 290°C with a maximum in the temperature range of 350-370°C. This is the interval of the dew point of ammonium chloride, that is, the point where ammonium chloride deposited in solid form from the gases and also probably the point where the dissassociation present at higher temperatures start. At the same time corrosion was increased here, since at this point water had to be injected in order to avoid plugging due to the deposition of ammonium chloride. The corrosion was a combined action of chlorine and sulfur; whereby, chlorine drilled holes and sulfur converted at the attached points to sulfides of the corroded elements. The corrosion product was always iron sulfide.
>
> None of the technically available metals was able to withstand the attack.
>
> Only tantalum liners were completely resistant, however this was impossible for commercial use.
>
> For a commercial operation, the attack had to be prevented chemically. The corroding medium was probably ammonium chloride itself, and not only free hydrochloric acid. Addition of ammonia

after the hot catch pot probably increased corrosion, although it reduced the concentration of free hydrochloric acid. In order to be catalytically active in the converter chlorine had to be present as ammonium chloride or dissociated ammonium chloride. Neutral compounds of chlorine which did not dissociated under reaction conditions since they had no catalytic activity. To a small extent, the chlorine is bound by the alkaline components of the coal ash (CaO, MgO). However, the neutralization is not complete since calcium as well as magnesium chloride is hydrolized by the steam which is present from the reduction of oxygen in the reaction space. The predominant amount of chlorine present in the converter is ammonium chloride (or in the form of its dissociation products).

It was, therefore, necessary to have free ammonium chloride present in the converter, and in the products leaving the converter chlorine that does not dissociate. This requirement was fulfilled by injecting into the gases and vapors that leave the hot catch pot a suspension of sodium carbonate in distillate heavy oil. The chlorine was bound as sodium chloride, and in a second hot catch pot, in which a constant level was maintained, was removed together with the distillate heavy oil as a residue. This was an additional complication but the difficulties were unimportant in view of the great catalytic effect of chlorine. The completeness of neutralization in hot catch pot II was observed readily by seeing a thin layer of black iron sulfide on the interface of water and catch pot product when chlorine was not completely neutralized.

On the basis of the observations of this corrosion one was afraid of having corrosion in the corresponding inner walls of the preheating system. Small scale experiments with coal throughputs of 50 kilograms of coal per day did not show any corrosion which corroborated results found in the ICI experiments in weeks of operation. The large scale experiment in Ludwigshafen with a throughput of 1500 tons of coal in three months showed only negligible attack in the preheater. As explanations for the absence of corrosion in the preheating zone, several possibilities were indicated:

1. Water, which is necessary for corrosion in the cooling zone, is present in the feed in only small concentrations compared to the concentration in the vapors and gases leaving the converter.

2. During preheating part of the chlorine reacts with the coal-ash and is then by the action of steam freed by dissociation in the converter.

3. The highly asphaltic oil in the preheating zone (asphaltine of the pasting oil and the predominant highly viscous primary reaction products of coal) form a protecting film on the walls of the preheater against the action of chlorine on the material.

This protecting film action of heavy oils had been found previously when the attack of corrosive agents on materials was tested. It was shown then that carbon steel withstands the attack of hydrogen and hydrogen sulfide better if the protective oil film is present. However, this does not prevent the attack completely and one cannot avoid the use of alloy steels."[34]

In this early German liquefaction development[35] they also modified the catalyst for bituminous coal liquefaction.

"It was found advantageous to change the iron catalyst used with brown coal by replacing part of the Bayermass by iron sulfate which was added in aqueous solution to the coal. This led to the neutralization of the coal ash and had as a result that chlorine present to 0.05 to 0.1% in practically every bituminous coal was freed and was not completely bound by the coal ash. It led to slight corrosion in the exit lines. To neutralize this chlorine small amounts of sodium sulfide (about 0.3%) were added to the coal which not only led to a complete neutralization of the chlorine but in addition had a favorable effect as a catalyst, (especially increasing the splitting)."

This experience is still being utilized in the FRG where Saarbergwerke utilizes a three-component catalyst in their liquefaction process development unit.[36] The catalyst consists of an aqueous ferric sulfate impregnation of coal, red mud, and sodium sulfide. One function of the sodium sulfide is to neutralize chloride in the coal. Saar coals typically have a chloride content of 0.4 pct. The other function depends on the alkalinity of the mineral matter in the coal. Thus different amounts are added for liquefying bituminous or lignite coals. Sodium sulfide addition also affects the pH of the water separated from the oils. The desired pH is 10-11 in the separator from which water is removed from the process.

Other FRG liquefaction processes under development, depending on the coal characteristics, are also using such an additive.[37] This might explain why there have been no reports of the significant corrosion problems with certain portions of the liquefaction plants, such as fractionation columns, dealing with essentially solids free hydrocarbon liquids. Certainly the foreign countries are well aquainted with this materials problem from U.S. experience, which appears to be associated with coals containing relatively high amounts of chlorine (>0.1%)[38] yet no such problems have been mentioned in the literature or during foreign visits.

Since the current German processes do not recycle the asphaltenes and preasphaltenes but appear to be planning to gasify the mineral ash residue, the chlorine problem may be transferred to the gasifiers. The introduction of higher sodium content feeds in the gasifiers may also aggrevate the refractory and/or heat recovery systems materials problems in the gasifiers.

Stabilization and/or upgrading of distillate oils derived from coal has been mentioned by several process developers but no materials information was found.

## 4.3 Summary of Materials Findings

For most of the countries the information on processes and materials of construction has been directed at internal usage based upon indigenous or available coal supplies. Thus as noted in the early part of this section application of materials information in the U.S. would require a matching of coal types as well as review of the process step details.

If they are to be useful, the experiences related in this document must be understood in the appropriate context. By comparison with commercial coal liquefaction plants, many of the units discussed are small. Some are based on first generation coal conversion technologies which tend to be limited in the size of individual process units; plant capacity is increased by adding parallel flow tains. The more advanced technologies are represented by sub-scale equipment, i.e., process development units and pilot plants. In general these liquefaction development units are not fully integrated pilot plants since they do not include hydrogen production from the mineral ash residue and upgrading of the coal derived oil products. Thus continuing modifications in process conditions and materials requirements can be expected.

Going to commercial size alone will introduce materials problems not encountered in smaller units. Large, thick walled vessels, for instance, will increase concerns relating to field erection, including heavy section welding, heat treating, inspection, and lower toughness as a result of the increased thickness. Certainly the process developers in the FRG feel that higher conversion pressures are desirable to improve process efficiencies and increase unit throughputs. Such increases will not only result in modifications to pressure vessel designs to fit available alloys but will also encourage development of new materials. Such increases in pressure will also aggrevate erosion/corrosion effects. The consequences relate primarily to coal feed components, reactor internals, and pressure let-down devices. Conversely, steady state operation at fixed conditions for relatively long run times will ease materials/environment interactions related to transients (which are typical of pilot plant operations). In general, then, the experience cited is not representative of large-scale, commercial operating conditions. Its value lies primarily in alerting designers/developers to potential problem areas and to some design alternatives that have been explored elsewhere. The most pervasive category of problems throughout the coal conversion technologies involve the materials-handling ancillaries. Conveyers, pumps, valves, and ducts used for coal feed, coal distribution, and ash removal are typically susceptible to erosion and wear ranging from significant to catastrophic. The other lessons that can be extracted from the review of overseas experience are not foreign to the findings of U.S. development programs.

Early establishment of the design/materials interface is important. Post-design fixes involving process parameter changes to suit a vulnerable component can have effects both upstream and downstream. System integration and optimization may be impacted. Early identification of trouble spots and system oriented resolutions should be emphasized.

Specific published information on equipment designs, materials choices, solutions to materials performance problems, or materials development programs is severely limited. To supplement the very limited published data, we have reviewed available foreign trip reports, interviewed foreign travelers, and made a limited number of contacts by letter. From these sources we have been able to establish the fact that materials choices and the associated equipment design information are in general proprietary. Each organization involved in developing a process or a system for incorporation into an overall liquefaction process appears to have at least a limited materials test program. While some are willing to discuss their test programs and at least some of the results, they have not published and are not planning to publish the information. Thus the most useful technical information on materials choice and performance in specific applications can only be obtained through appropriate contacts with materials personnel or design engineers at the various process development organizations. In general this implies a visit to the appropriate organization. Such visits were beyond the funding of this assessment. We feel that continued interchanges of materials information is imperative and materials experts should be included in any foreign reviews of liquefaction developments. Two process development areas appear to offer significant materials information potential in the near future. These are the entrained gasifier developments of the Texaco and Shell-Koppers in the Federal Republic of Germany and the direct liquefaction plant at Bottrop in the FRG. Particular attention should be paid to the effects of the German additions of sodium to the coal liquefaction process and its subsequent effect on the gasifiers.

## 4.4 References

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