CALCIUM CARBONATE DEPOSIT FORMATION DURING THE LIQUEFACTION OF LOW RANK COALS

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Introduction

During the liquefaction of low rank coals, that is subbituminous or lower, the calcium humates in the coal decompose to form calcium carbonate solids. These solids have been identified in the reactor solids from pilot plant runs and could be a significant operational problem in commercial sized equipment. The purpose of this paper is to present our operating experience and proposed solutions to this problem as it applies to the Exxon Donor Solvent, or EDS, Process. The units used in the EDS development program range from 3 gram batch reactors to a one ton-per-day process development unit.

In the EDS Process, which is shown in Figure 1, crushed coal is slurried with a hydrogen donor recycle solvent and liquefied in a tubular upflow reactor to which molecular hydrogen has been added. The liquefaction operating conditions are about 840°F and 2000 psig. The liquefaction reactor product is separated into a light hydrocarbon gas stream, the spent solvent, which is recycled and upgraded in a catalytic hydrogenation unit, the total liquid product and a residual bottoms slurry which is processed in a Flexicoker to produce process fuel and some additional liquid product. The ash residue from the Flexicoker is landfilled. The plant is balanced in that the solvent, hydrogen and process fuel needed are generated by the process. For an Illinois No. 6 bituminous coal approximately 2.7 barrels of liquid are produced per ton of dry coal. Liquid yields from a balanced plant processing lower rank coals are less because of their lower carbon content.

Source of Calcium Carbonate Deposits

Most of the calcium in low rank coals is in the form of salts of humic acids. These calcium humates are represented in Figure 2. These humates decompose in the liquefaction reactor to form calcium carbonate. The exact mechanism for calcium carbonate formation is not known, but all of the components of the calcium carbonate within the dashed lines are readily available. The calcium is ionically bonded to carboxylic acid and sometimes phenolic groups in the coal. Since these groups are weak acids, the calcium can be ion-exchanged. There are also other calcium salts present in coal. Calcite and gypsum are found predominately in higher rank coals, bituminous and above, and are stable under liquefaction conditions. The three coals studied in greatest detail for calcium carbonate deposition are: a Wyoming subbituminous coal from the Wyodak mine, a North Dakota lignite from the Indian Head Mine and a Texas lignite from the Big Brown Mine.

Identification of Calcium Carbonate Problem

During the second quarter of 1975, a screening study was completed on the Wyoming subbituminous coal. Inspection of the reactors used in these runs revealed calcium carbonate deposition as wall scale. Since this was not a problem specific to the pilot units used, calcium carbonate deposition could have a significant impact on the operation of a commercial unit. A study was then initiated to identify the magnitude of this deposition problem.

The bench scale and pilot units used in the calcium carbonate deposition study range from 3 gram batch tube autoclave reactors to a one ton-per-day Pilot Plant. Each of these units plays an integral part in the testing of solutions to the calcium carbonate problem. Some solutions can easily be tested in the batch reactor; whereas other solutions must be tested in a flow unit. The liquefaction product from the batch reactor is separated with a hydrocarbon solvent wash and the residue is analyzed for calcium carbonate by X-ray diffraction and thermo-gravimetric analysis. In the flow units, the residual bottoms can be tested similarly as in the batch case. But more importantly, the reactor solids from these units can be analyzed for particle size, calcium carbonate content and calcium carbonate growth patterns and crystal forms. The larger units, the 50- and 100-pound-per-day Recycle Coal Liquefaction Units (RCLU) and the one ton-per-day Coal Liquefaction Pilot Plant (CLPP), are completely integrated pilot plants with distillation and recycle solvent hydrogenation sections. A smaller Once-Through Coal Liquefaction Unit (OTCLU) uses a simulated recycle solvent and has no distillation or solvent hydrogenation facilities.

Types of Deposit Forms

Calcium carbonate deposition occurs as scale on the liquefaction reactor wall and free-flowing solids or oolites. Wall scale is very easy to detect in the liquefaction reactor solids by its characteristic shape. Oolite solids are particles of the coal mineral matter, clays, silicas, etc., which have a uniform layer of calcium carbonate growing around them. These oolites are predominately concentrated in mesh size fraction one size larger than the feed coal. For example, in the small pilot plants which use minus 100 mesh coal, the oolites are concentrated in the 50 to 100 mesh size. Similarly, for the large pilot plant using minus 30 mesh coal, the oolites are concentrated in the 16 to 30 mesh range. These oolites would be expected to grow larger during much longer runs, because they would not be swept out of the reactor by the normal fluid flow.

The predominant form of the calcium carbonate growth does depend on the coal from which it was formed. With the Wyoming subbituminous coal, the wall scale formed is primarily vaterite which is rarely found in nature. The growth on the oolites is primarily calcite and some wall scale, at times, is also calcite. For North Dakota lignite, on the other hand, scale and oolites in the first stages of the reactor are always calcite and in the latter stages of the reactor sodium magnesium carbonate (eitelite). The forms of the calcium carbonate deposits for the Texas lignite are essentially the same as those for the Wyoming coal.

Most of our operating experience with low rank coals has been the processing of Wyoming coal in the 50 pound-per-day RCLU pilot plant. After a run in this unit the reactor is removed and drained of solids and residual coal slurry. Methyl ethyl ketone washes and sometimes mechanical scraping are needed to remove the scale. The total solids are toluene washed to remove excess solvent, dried and sieved. For the RCLU unit, the wall scale is plus 50 mesh. Oolites are 50 to 100 mesh. Minus 100 mesh material is unreacted feed coal or coal mineral matter which has not yet formed oolites. The ranges of accumulation of calcium carbonate containing solids for the three coals studied are shown in Table 1. The accumulation is reported as pounds per 100 pounds of coal fed to compensate for the variations in run length. The only significant difference in the three coals is that the Texas lignite produces more oolites than the Wyoming coal. The oolite accumulation for the North Dakota lignite is not available because it was not possible to accurately sieve the reactor solids. The deposit accumulation is unaffected by changes in most liquefaction process variables, such as, temperature, space velocity, solvent quality, solvent boiling range and hydrogen gas rate. During high pressure operations (2500 vs. 1500 psig) there was a significant increase in oolite and wall scale accumulation.

Scanning Electron Microscope (SEM) photographs have provided invaluable information about the reactor solids recovered from the flow units. Most of the oolites have surfaces of calcium carbonate. This is identified by an X-ray spectrometer which is an integral part of the SEM. Some oolites have surfaces of iron sulfide crystals which are again identified by the X-ray. The iron sulfide surface is much more irregular in appearance than the calcium carbonate surface. Cross sections of these oolites reveal more information about the calcium carbonate growth. These cross sections show that calcium carbonate growth occurs on seeds of the coal mineral matter. There is also evidence of iron sulfide growth on the mineral matter seeds. The seed material can be iron sulfide itself, silica or clays or any part of the coal mineral matter. The iron sulfide growth is very regular and crystalline whereas the calcium carbonate growth is more evenly distributed.

The other type of calcium carbonate growth is wall scale. The reactor used in the 15 pound-per-day OTCLU is very amenable for detecting scale. It is a vertical hairpin tubing reactor which can be split along its length for a detailed inspection of any scale present. The reactor which is shown schematically in Figure 3 has eleven sections: six upflow and five downflow. The graph at the bottom of Figure 3 is a plot of the amount of calcium in the wall scale versus the reactor section number. Almost all of the calcium carbonate scale is in the first half of the reactor with the heaviest concentration in the 15 to 25 minute residence time range. This finding has been verified directionally in the pilot plants, although it is very difficult to detect the exact location of scale in the pilot plants. The SEM can also be used to detect the structure of the scale. The surface of the scale which is next to the reactor is smooth and is mostly iron sulfide and a slight amount of nickel sulfide. This is indicative of the fact that the sulfidation products of the wall are providing growth sites for calcium carbonate. The process side of the scale has a surface which is very similar to that of the oolites.

Solutions to Deposition Problem

Potential solutions to calcium carbonate deposition that we have investigated are mechanical or chemical in nature. The mechanical solutions tried are solids withdrawal and acid washing. The theory behind solids withdrawal is that since the oolites are free-flowing solids it should be very easy to withdraw them from the liquefaction reactor. Oolite growth can be controlled if the withdrawal rate is high enough so that the oolites do not have sufficient residence time for growth. Solids withdrawal has been very effective in controlling the growth of oolites in the one ton-per-day unit. A way to control wall scale growth is periodic acid washing of the reactor walls during reactor shutdowns. Several chemicals have been identified as ones which can effectively dissolve the calcium carbonate scale. A combination of solids withdrawal and acid washing is a very cost effective way of controlling calcium carbonate deposits. An uncertainty here is whether the scale would flake off the reactor walls and cause operational problems during the extended runs (6-12 months) in a commercial plant. This uncertainty will be tested during the operation of our 250 ton-per-day pilot plant now under construction.

The effect of solids withdrawal on solids accumulation and oolite growth in the one ton-per-day unit is shown in Table 2. During a four-day run without solids withdrawal, 1/4 percent of the coal fed remained in the reactor and of this amount, about one-third was larger than the feed coal, that is, plus 30 mesh. During a 16-day run with solids withdrawal, only nine-hundredths of one percent of the coal remained in the reactor, and essentially none of the oolites grew larger than the feed coal. Wall scale growth rates were about the same for both runs. This scale growth would amount to about 1/2 inch per year.

Chemical solutions to the calcium carbonate deposition problem can be classified as coal pretreatments or reactor additives. Coal pretreatments are ion exchanges in which the humate calcium which is the source of the calcium carbonate deposition is reacted with acids or metal salts. The resulting calcium salt would, of course, need to be stable in the liquefaction reactor for the exchange to be successful. A generalized mechanism for the ion exchange is:

$$MX \rightarrow M^{+2} + X^{-2}$$

$$M^{+2} + \sim Ca \sim \rightarrow \sim M \sim + Ca^{+2}$$

$$Ca^{+2} + X^{-2} \rightarrow CaX$$

Where the $\sim Ca \sim$ is a representation of the humate calcium.

The acids that we have concentrated most on and have been successful in ion exchanging with the calcium are sulfuric acid and sulfur dioxide. The sulfur dioxide readily dissolves in the coal's moisture and forms sulfurous acid. The HSO_3^- ion then diffuses through the coal pores to the site of the humate calcium where it exchanges with the calcium. Various metal salts have also been tried. In general, bivalent metal salts exchange very effectively with the humate calcium. Monovalent metal salts will also exchange if the resultant calcium (CaX) salt is very insoluble. For example, sodium carbonate will exchange more effectively than sodium sulfate because the resulting calcium carbonate is more insoluble than calcium sulfate. This insolubility provides an added driving force for the exchange. The metal salts would have an added advantage if the metal were catalytically active in liquefaction.

Coal pretreatments can be tested in the batch tube autoclave reactor because the form of the calcium has been changed, and it is only necessary to determine the amount of calcium carbonate in the liquefaction residue. Untreated Wyoming coal forms about 40% calcium carbonate on ash. Sodium sulfate is only partially effective in ion-exchanging with the calcium. The liquefaction residue contained about 20% calcium carbonate on ash (the remaining calcium is calcium sulfate). A run in the 15 pound-per-day unit did produce scale which confirms that sodium sulfate is only partially effective. Sulfur dioxide treated coal has only about 8% calcium carbonate on the ash of the residue. Ferrous sulfate and sulfuric acid are even more effective in exchanging with the calcium. After these pretreatments there is only 1% calcium carbonate in the residue ash. Reactor inspections after runs in the 15 pound-per-day unit revealed no scale for the sulfur dioxide, ferrous sulfate and sulfuric acid pretreatments. Sulfur dioxide and sulfuric acid treatments were also successful in preventing scale and oolite growth in the 50 pound-per-day RCLU.

Liquefaction reactor additives have different proposed mechanisms for success, but in general are not fully effective. Surfactants theoretically will disperse the calcium carbonate into a fine size so that it will flow out of the reactor before forming scale. It was difficult to find a surfactant that was stable under liquefaction conditions, but when we tried one that was, it had no effect on scale growth. There are two types of scavengers used: One to tie up the calcium, for example, collodial silica to form calcium silicate, and another to scavenge the carbon dioxide, for example magnesium oxide. Neither of these materials was effective in preventing calcium carbonate growth. Another possible mechanism for the colloidial silica to work is by providing many small sites for the calcium carbonate growth. This could prevent wall scale growth. Addition of two weight percent colloidial silica on coal did reduce scale formation in the 15 pound-per-day unit but did not eliminate it. Crystal modifiers have been used to shift the crystal form from vaterite to calcite but have had no effect on scale growth. Some reactor additives which have shifted the Wyoming coal wall scale from

vaterite to calcite are water, hydrogen sulfide and various chelating agents. The basic reason for the failure of these reactor additives is that the calcium carbonate formation occurs in the pores of the coal, and reactor additives reach only the coal particle surface at best.

SUMMARY

The major findings in our liquefaction work with low rank coals are that oolite formation and wall scale growth are primarily related to coal rank. We have detected both forms of calcium carbonate deposits with every low rank coal tested. As long as the calcium in the coal is present in the humate form, calcium carbonate deposition will occur. The physical withdrawal of solids from the liquefaction reactor can effectively control oolite accumulation and growth but not wall scale. Wall scale can be removed during reactor shutdowns by acid washing. Liquefaction reactor additives are generally ineffective in controlling calcium carbonate deposition. Coal pretreatment, that is, ion-exchange, can be very effective in altering the form of the calcium salt and thus prevent any type of calcium carbonate deposition in the liquefaction reactor.

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TABLE 1

RANGES OF CALCIUM CARBONATE SOLIDS ACCUMULATION

COAL TYPE	WYOMING SUBBITUMINOUS	NORTH DAKOTA LIGNITE	TEXAS LIGNITE
MINE	WYODAK	INDIAN HEAD	BIG BROWN
COAL COMPOSITION, WT% DRY COAL			
CALCIUM	1.22	1.31	2.2
SODIUM	.05	.84	.05
SOLIDS ACCUMULATION, LBS/100 LBS COAL FED			
TOTAL SOLIDS	0.35-0.57	0.22-1.1	0.49-2.0
OOLITES	0.07-0.27	NA	0.39-0.49
WALL SCALE	0.002-0.007	0.005-0.035	0.002-0.010
TOTAL SOLIDS COMPOSITION, WT%			
ASH	56-70	57-67	78-82
$CaCO_3$	24-83	17-49	67-74
$Na_2Mg(CO_3)_2$	-	24-46	-
$CaCO_3$ FORMS	CALCITE, VATERITE	CALCITE	CALCITE, VATERITE

TABLE 2

EFFECT OF SOLIDS WITHDRAWAL ON SOLIDS ACCUMULATION ONE TON-PER-DAY UNIT, WYOMING COAL

	WITHOUT SOLIDS WITHDRAWAL	WITH SOLIDS WITHDRAWAL
INITIAL SOLIDS ACCUMULATION, WT% OF FEED COAL	0.25	0.09
PARTICLE GROWTH WT% OF REACTOR SOLIDS LARGER THAN FEED COAL	33	1
WALL SCALE GROWTH INCHES/DAY	.001	.0011-.0015

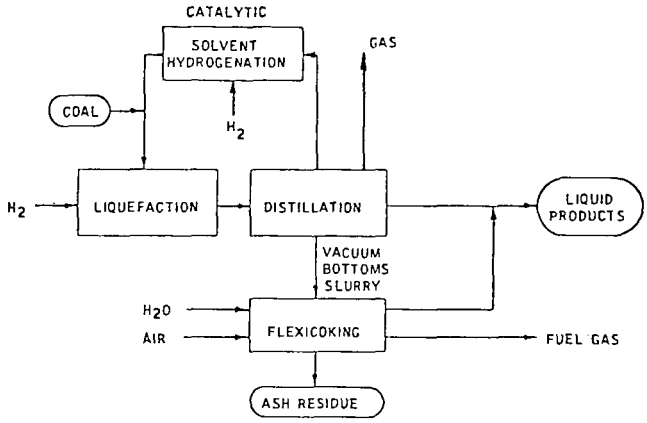

FIGURE 1. EDS PROCESS SCHEMATIC

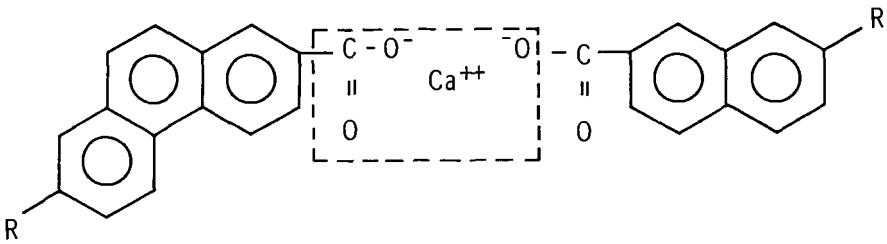

FIGURE 2. REPRESENTATION OF CALCIUM HUMATES

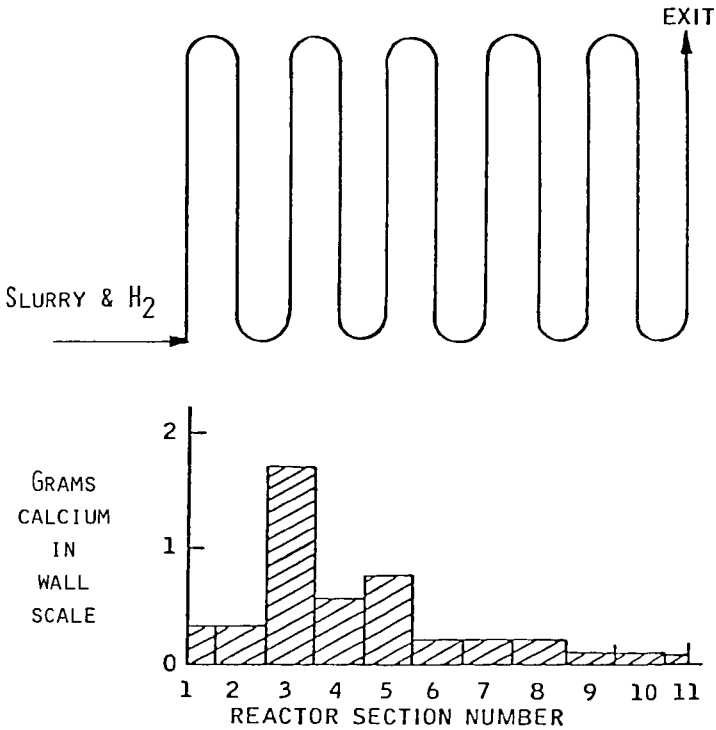

FIGURE 3. SCALE DISTRIBUTION IN A 15 LB/DAY UNIT