CATASTROPHIC OXIDATION

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Catastrophic oxidation is an unusual and unpredictable form of deterioration experienced in three Kellogg built plants. Specifically, it was experienced in one ammonia plant (primary reformer transfer line) and in two ethylene units (pyrolysis furnace transfer lines). This form of attack occurs on Type 316 stainless steel which, to refresh your memory, is the 18 chrome-8 nickel grade with approximately 2% molybdenum content for added strength and corrosion resistance.

Figure 1 shows a piece of an elbow taken out of a pyrolysis furnace transfer line; it probably ran approximately 50°F hotter than most reformer plant transfer lines. I do not remember the exact wall thickness of this line—it was probably between 1/2 and 1 in. Note that it is completely perforated in one area and that the surface is heavily encrusted with a loosely adherent oxide scale. The small piece shown on the left is a porous oxide plug which had formed directly over the hole. Figure 2 shows a cross section of this plug, revealing the stratified friable nature of this oxide layer. As is evident by visual inspection, this particular oxide scale is highly pervious and nonprotective.

"Go—no go" type behavior

Figure 3 illustrates a failure experienced in a primary reformer outlet line. The photograph shows the pipe after sandblasting; it too was heavily encrusted when removed from service. The failure of this 5/8-in. wall pipe occurred within less than a year. It is exceptional indeed to find such a marked "go—no go" type behavior in high temperature corrosion experience, where the metal either corrodes very severely or remains essentially unaffected. This is quite an unusual phenomenon and differentiates ordinary from catastrophic oxidation.

With ordinary oxidation, there is fairly uniform attack, although hot spots cause heavier scale deposits and may lead to eventual perforation. Nevertheless, metal loss is reasonably uniform and devoid of such sharp demarcation between areas of attack and no attack. This characteristic of catastrophic oxidation is related to the mechanism of attack, specifically to the formation of liquid slags or even volatile phases.

Accelerated corrosion

The term catastrophic is of course very apt and I would like to add, was not coined by us to strike fear into people's hearts. The term had been in use for some time among corrosion specialists to denote a form of attack characterized by an inverse time dependency, i.e., metal is consumed at a progressively increasing rate. For this reason, some persons prefer the word accelerated corrosion which is perhaps more precise but not nearly as picturesque. The resulting high rate of attack can be of extreme magnitude, creating a veritable runaway condition. Scattered experiences have been reported with corrosion rates as high as 9 ft./yr. which is equivalent to holing through an automobile muffler in 3 hr.

Fuel ash corrosion

Many of you are undoubtedly familiar with a more widely publicized form of catastrophic oxidation called fuel ash corrosion. It is encountered in fur-

Figure 1. Large piece is perforated Type 316 stainless steel elbow section from naphtha pyrolysis furnace outlet line. Small round chunk is a porous oxide plug which had formed directly over hole. Also shown is a square piece of soot-contaminated asbestos insulation.

Figure 2. Cross-sectional view of bulky oxide plug shown in Figure 1. Stratified appearance and friable nature of corrosion product is characteristic of catastrophic oxidation.

naces, boilers and turbines exposed to flue gases from residual fuel oils which are contaminated with certain metallic compounds. The most troublesome constituents identified in fuel ash are vanadium pentoxide and sodium sulphate, which form low melting point slags (approximately 1,130° F) that are extremely aggressive to all engineering alloys.

In the case of fuel ash attack, this corrosive slag is produced solely from substances in the environment. With catastrophic oxidation of Type 316 stainless steel, molybdenum oxide, the most important slag ingredient is derived from an alloying constituent in the metal itself. In either case, the degradation is closely associated with the presence of low melting point or even volatile phases rich in oxides of certain refractory metals (Mo, V, W).

Oxides form eutectics

These oxides may form eutectics with other substances, resulting in further lowering of melting points. One of these is the eutectic of molybdenum trioxide and sodium oxide, which has a melting point below 1,000° F. This particular one is of special interest because we suspect that the specific failures shown here have been caused by this or some similar eutectic.

It is conjectured that the sodium oxide was produced by thermal degradation of sodium silicate. Sodium silicate is frequently used as a binder in high temperature insulation materials and in the water glass pastes used in their assembly. It is ironic that prior to this experience, we actually favored insulations con-

taining silicates due to their ability to inhibit stress corrosion cracking of austenitic alloys.

Corrosion and contamination

The literature reports that catastrophic oxidation of molybdenum containing alloys can happen without the presence of contaminants such as silicates. The mechanism of attack is then associated with the formation of gaseous molybdenum trioxide in the stagnant zone which ordinarily exists between the insulation and the underlying metal. However, there is limited experience indicating that catastrophic oxidation at relatively low temperatures is not caused solely by stagnation but requires some activating surface contaminant.

Catastrophic oxidation of Type 316 stainless steel is not only a rare but also an unpredictable phenomenon. The majority of experiences reported have been fuel ash corrosion by high vanadium fuel oils and are not specifically connected with molybdenum alloys. In the absence of environmental contaminants, catastrophic oxidation of molybdenum containing alloys is considered quite unusual except with alloys appreciably richer in molybdenum than Type 316 stainless steel, or at considerably higher temperatures. Further evidence of the elusive character of catastrophic oxidation is that laboratory tests by us and others fail to induce attack under simulated reformer furnace conditions.

Rule-of-thumb recommendations

In conclusion there are several rule-of-thumb recommendations for preventing catastrophic oxidation.
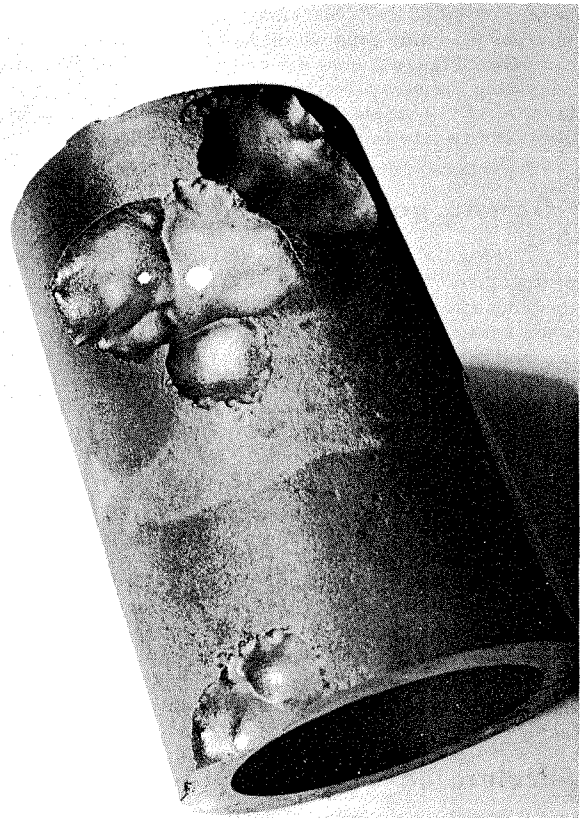

Figure 3. Catastrophic corrosion of insulated Type 316 stainless steel reformer furnace outlet pipe. Sandblasting clearly reveals sharply demarcated zones of attack associated with localized formation of molybdenum oxide rich slags.

First, observe scrupulous cleanliness—any surface contaminants should be removed, which incidentally is a good idea with all stainless steels and high nickel alloys. Second, do not insulate—since this is admittedly quite impractical in most instances; insulation materials should be limited to those free of potentially flux forming ingredients such as sodium silicate. Finally, the use of Type 316 stainless steel can, of course, be avoided altogether in favor of molybdenum-free alloys. Replacement of Type 316 stainless steel in existing units would be difficult to justify because catastrophic oxidation is after all an unusual occurrence and apparently controllable by using compatible insulation materials.

DISCUSSION

Anonymous: Was there any weld slag contamination in the area of the failure?

SORELL: No. We don't think this was caused by such slags because we check for this possibility. For your reference, the serious problem of weld slag corrosion has been reported in a paper by Tidewater Oil Co. Speaking of contaminants, I would like to reemphasize that there are certain insulations considered compatible and others that are not. The compatible grades would be those that have neither silicates nor other substances that could promote fluxing. Evaluation of suitable insulations is largely a measure of trial and error and past experience. On this basis, it is our opinion that insulations containing sodium silicate should be prohibited.

Anonymous: One other question. The reaction temperatures that are required with iron oxide, sodium oxide, and calcium silicates, would be up around 900° C, would they not? Can you reach these temperatures?

SORELL: I think that some of these failures can occur at 1,300 or 1,400°F. As I mentioned, certain eutectics of sodium oxide and molybdenum oxide melt in the neighborhood of 1,000° F.

WALTON—SunOlin: On these failures of 316 transfer lines, where you suggest removing insulation periodically and looking for possible trouble, removing all the insulation from a transfer line can be a very expensive proposition, and on our coming shutdown we're planning to remove 2-ft. sections, every 15 or 20 ft. Would you consider this a satisfactory way to look for this phenomenon likely to occur at spots and not in others?

SORELL: Fortunately catastrophic oxidation has not occurred with such frequency that I can consider myself any kind of an expert. Considering however the highly sporadic nature of attack, spot checking will not give you positive assurance that you are not experiencing attack in adjacent portions.

Anonymous: I heard that some of this trouble comes from manganese in 316. Is that entirely false?

SORELL: I believe it is. It's molybdenum.

DESSO—Southern Nitrogen: This catastrophic oxidation can happen at temperatures that you have in your secondary reformers. In fact we lost a 310 stainless steel liner with this type of oxidation.

SORELL: The higher the temperatures, the more likely it is that attack can occur. Type 310 stainless steel is a 25 Cr-20 Ni composition which does not normally contain molybdenum. However, there are some grades that do, especially certain welding electrodes. It may be, therefore, that you may have some molybdenum containing Type 310 stainless steel without realizing it. Could that have been the case?

DESSO: This happened to us very soon after we lost the bed in one of our activated carbon drums and actually blew carbon completely through into the secondary reformer. Probably our culprit was the caustic residue from the activated carbon after it was burned.

SORELL: As I mentioned before in connection with fuel ash corrosion, it does not necessarily have to be molybdenum but can also be some contaminant in the atmosphere. If you have sodium compounds present, especially at these very high temperatures in the secondary, they may possibly form certain slags which could initiate attack.