

# Bulletin Board

## Seminar Offerings

### 14th Annual All Users Conference

Innovative Techniques for  
NDE Boiler Inspection

#### Reach Resort Key West, Florida

Jan 6,7,8 2009

UDC and DNFM are proud to announce our newest service **Linear Phased Array**. This cutting edge technology will revolutionize the way our industry conducts NDE procedures. Come see for yourself in beautiful Key West, Florida.



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#### Snowbird, Utah

Feb 27- March 3rd, 2009

Our unique inclusive joint approach shares principals which highlight the concerns of power plant staffing. Join us and see why clients find our seminars "Pioneering and Informative"



Register Early and Save \$\$\$\$\$

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## View From the Penthouse Fall Edition 2008



Deposit may be layered, with red hematite iron oxide

### Phosphate Corrosion

Corrosion by phosphates is an on-going problem in phosphate-treated boilers, especially as pressures have increased. Sodium phosphate is used to buffer boiler water pH. "Congruent control" with phosphates was introduced to prevent the formation of free caustic, but the phosphate compounds have interacted with deposits and corrosion products and precipitated within deposits. These phosphates hideout in deposits as temperatures increase. The equilibrium chemistry for the phosphates depends on the boiler pressure and on whatever other additives are present in the water, so the treatment program needs to be tailored to the individual boiler conditions.

Phosphate corrosion results in localized attack under deposits, producing gouges, grooves or depressions similar to those resulting from caustic. Hideout is associated with increased pH in the boiler water, so high-pH related corrosion may be reported even though the conditions within the deposits may be acidic. Thus, phosphate corrosion is frequently confused with caustic attack. Careful analysis of deposits is needed to confirm that acid phosphate attack has occurred.

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# View From The Penthouse

The David N. French Metallurgists Newsletter

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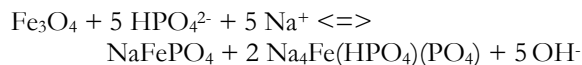
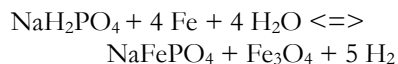
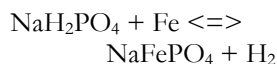
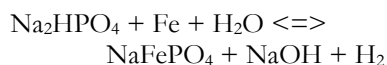
Dr. David C. Crowe

## Mechanism

The attack occurs where a deposit or scale has already formed. Chemical conditions within the deposit can be significantly different from the bulk water due to restricted mass transport. Some impurities can concentrate within the deposit. Additionally, the deposit acts as an insulator, resulting in higher temperatures on the waterside surface. Sodium phosphate salts have retrograde solubility, that is, they precipitate from solution as the temperature increases. Higher temperatures within deposits present conditions for precipitation of phosphate salts. Consequently, the phosphates hideout in the deposits. The magnetite in the deposit provides a reactant that is believed to combine with phosphate, producing maricite, a sodium iron phosphate.

Phosphate concentrates in the deposit as the temperature increases, and the pH drops perhaps to the range of 5 to 5.5 depending on the level of concentration. High quality steam forms or steam blanketing occurs due to the heavy deposit build-up. Within a deposit, wick boiling may occur, with water being drawn in at some point and steam vented elsewhere, and with phosphates depositing and concentrating. As temperatures increase in a boiler, the first place to hideout will be within deposits. The temperature increase may be localized where the heat flux is higher, and this is where deposits may already have collected. For this reason, hideout is a localized phenomenon.

The phosphate may react with the iron and magnetite to form maricite, NaFePO<sub>4</sub>. The reactions depend on the Na/PO<sub>4</sub> ratio and the temperature. Some reactions have been proposed:



Mono- and di-sodium phosphates have been shown to be the cause of phosphate corrosion, not tri-sodium phosphates. Hydroxides formed in these reactions could dissolve iron or magnetite under the deposit.

In phosphate corrosion, there is typically a porous deposit with an inner layer of the deposit which is white or grey. This light-colored compound may appear to be crystalline and can be identified via X-ray diffraction as maricite. Reddish streaks of hematite may also be present in the deposit. Iron phosphate may also be found. The solubilities of all the iron products except maricite appear to increase with decreasing temperature, so these corrosion products re-dissolve in the boiler water as it cools. This re-dissolution could release acidity. Alternating alkaline and acid conditions may be responsible for the layered appearance of corrosion products associated with this mechanism of corrosion. An outer layer on top of the corroded area typically contains porous magnetite particles and elemental copper particles.

## Differences with Caustic Corrosion

- In acid phosphate corrosion, the scale contains maricite, NaFePO<sub>4</sub>. In the case of caustic attack, there are no phosphate-containing corrosion products but sodium ferroate, NaFeO<sub>2</sub> may be present.
- No magnetite is found on the corroding surface with phosphate corrosion.

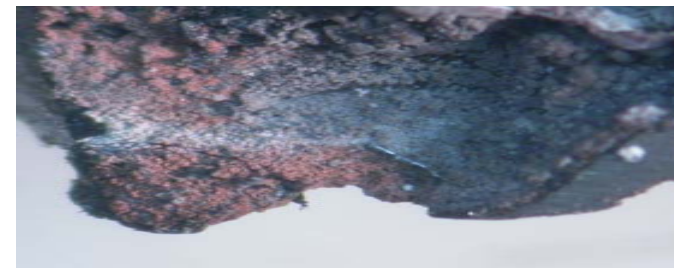
- The ratio of sodium to phosphate (Na/PO<sub>4</sub>) is different. If the ratio is more than 3:1, then caustic corrosion may occur. If the ratio is less than 2.3 at 600° F or 2.7 at 680° F, then acid phosphate corrosion may result. The ratio shifts the equilibrium from one type of phosphate to another, accompanied by a pH shift. The ratio at which caustic or phosphate corrosion occurs may be affected by other chemical additions and by temperature. Load swings can make control difficult.

## Deposit Analysis

Deposits may be analyzed via energy dispersive spectroscopy in the scanning electron microscope to obtain the weight percentages of elements that are present. This is a semi-quantitative measurement. Deposits will be rich in Na, Fe and P. EDS does not identify the compounds (mineral forms) that are present, however, the Na/Fe/P ratio may be consistent with maricite. If light-colored crystalline maricite deposits are found beneath the porous and friable outer part of the deposit, they may be confirmed as maricite via X-ray diffraction.

## Prevention

1. Maintain equilibrium phosphate control.
2. Chemically clean the waterside to remove deposit build-ups.
3. Reduce flow disruptions in tubes.
4. Reduce burner impingement.



Porous and friable deposit.

## Topic Ideas ?

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