VANTOM: Vanadium induced corrosion of boiler in partial oxidation process

M. Schmahl, X. Montero, C. Beyer, M. C. Galetz
e-mail: mathias.schmahl@yara.com
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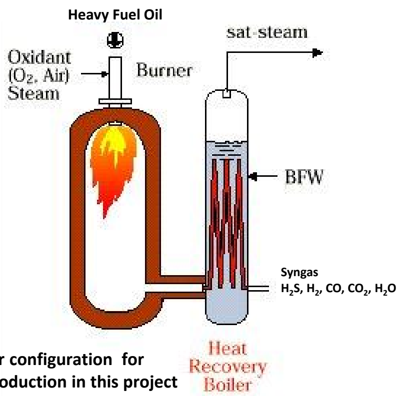
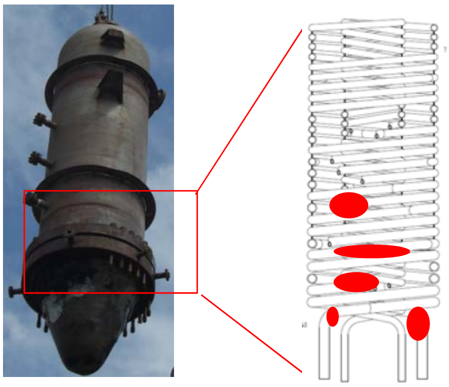
Introduction

- Heavy fuel oils containing vanadates are used for the production of syngas (H_2S, CO_2, H_2O, H_2, and CO) via partial oxidation (POx)
- Vanadates corrosion is also known from other combustion processes which burn heavy fuels, e.g. aircraft and marine turbines or fluidized bed
- Vanadate salts melt at low temperatures (around 600°C) accelerating hot corrosion by fluxing of the protective scales



POx boiler configuration for Syngas production in this project

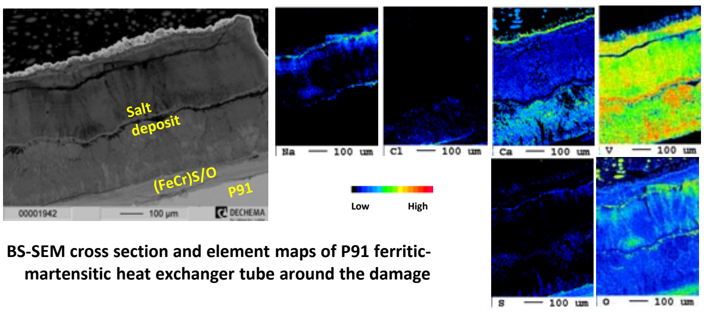
- Aim of this work: To understand vanadium corrosion in boilers working at low PO_2.
  - Heat exchanger coils manufactured from low alloy CrMo steel (10CrMo9-10) containing ferritic steel
  - Exposure temperatures range between 450°C and 600°C
  - Resulting good metal losses up to 5.3 mm.year^{-1} produce holes in the heat exchanger after less than two years



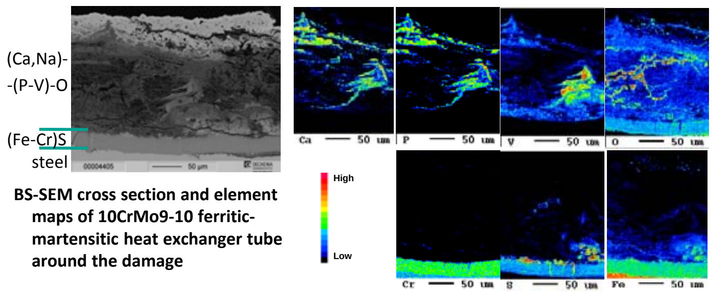
Usual damaged heat exchanger localization

Failure case analysis

In the area where the hole is produced a combined effect of sulfidation and molten vanadate corrosion is observed. The corrosion product is a three layered structure formed by CrS on the bottom, FeS in the middle, and a (Ca,Na)-(P,V,Cl) oxide on top, which contains Fe dissolved from the FeS layer.

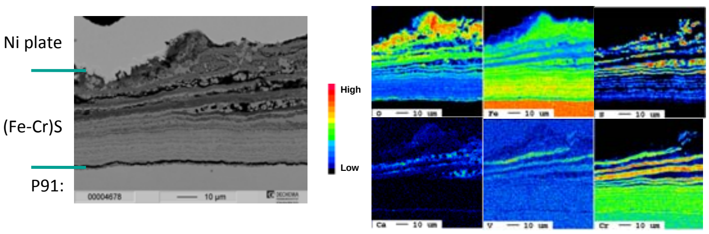


BS-SEM cross section and element maps of P91 ferritic-martensitic heat exchanger tube around the damage



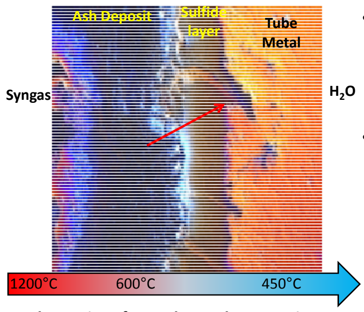
BS-SEM cross section and element maps of 10CrMo9-10 ferritic-martensitic heat exchanger tube around the damage

Not far from the position where the hole is produced also spots are found without deposit where sulfidation is detected as main corrosion issue. The corrosion produces a multiple layered structure which combines successively FeS and CrS.



BS-SEM cross section and element maps of the P91 ferritic-martensitic heat exchanger tube at 1 m distance of the hole/damage in the direction of the tube

Corrosion mechanism under different salts



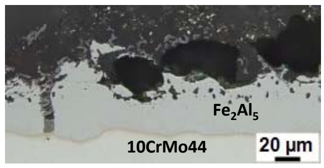
Schematics of vanadate salts corrosion

- NaCl combination is the most corrosive case. Active oxidation is the corrosive mechanism. Intergranular attack and evaporation of substrate elements increase the metal recession.
- The sulfate-vanadate hot corrosion is predominantly determined by the acid-basic constituents (Na_2O, V_2O_5 and SO_3). Pit formation increases with addition of Na_2SO_4. The main corrosion mechanism is the sulfidation followed by the dissolution and precipitation of oxide in the salt deposit.

Proposed solution

- The internal wall of a heat exchanger tube was coated with Al-based slurry (cost-oriented solution)
- Complete upscaling of laboratory-developed coatings was achieved following the steps below

Al coating produced by diffusion of slurry



Surface pretreatment
– Sand blast
– Etching and passivating

Slurry application
– Al and AlSi

Slurry drying
– Heated air
– Turning

Coating heat treatment
– 3 tubes in Ar
– 1 tube in air

Coating inspection
– Visual
– Endoscopy
– Tightness

Steps necessary for coating a heat exchanger inner wall and corresponding images

Prospects and outlook

- Corrosion decreases by reducing oxygen partial pressure
- Coatings performance AlSi slurry>Al slurry>No coating
- Coatings performance can be increased by addition of Ca based inhibitors
- New tubes can be coated (life time increase)
- Old tubes have been repaired and recoated (material recycling)
- Coated heat exchanger has been in service since 17/06/2016

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