Fuel Additives

The problem

- Corrosive combustion by-products and low melting point compounds when using crude and heavy oils and coal for the firing of boilers, furnaces and gas turbines.
- Corrosive by-products by decomposition of lubrication oils and by combustion of fuel in internal combustion engines (e.g., automotive, marine)

Boilers are an integral part of industrial activity and are widely used as a means to indirectly heat or vaporize liquid streams. The most widespread application is power generation where boilers are used to generate steam that is used to drive steam turbines and produce electricity. Most other relevant boiler applications involve generation of utility hot water or steam in the chemical and petrochemical industry. A familiar application example is P&P mill boilers.

Gas turbines are driven by air instead of steam and are used to drive electric generators. The air is mixed with fuel and ignited internally to produce a high temperature and pressure gas.

Heavy fuel oil and coal contain significant amounts of sulfur (S). Combustion of the fuels leads mainly to the formation of SO₂ as well as small amounts of SO₃ in the combustion flame. However SO₃ quantity can be further increased by the catalytic oxidation of SO₂. When the combustion gas temperature is lowered below its dew point (for example in boilers this may happen inside the economizer and air heater), SO₃ will convert to sulfuric acid (H₂SO₄) which damages metal surfaces. This type of corrosion is usually called cold or low-temperature or cold-end corrosion. An additional corrosion issue is a visible “plume” of acid aerosols when the flue gas exits the stack which can damage surrounding metal constructions and vehicles (acid smudges).

Fuel oils also contain Vanadium (V) and sodium (Na). Upon combustion these impurities react to form sodium vanadates (Na₂O·xV₂O₅), a component of the fuel ash or soot. These vanadates are low melting point phases and at high temperature deposit and stick onto the equipment internal surfaces (slag formation). Being potent corrosives, they cause significant damage to the metal surfaces. This type of corrosion is usually called high-temperature or hot corrosion.

Finally, in internal combustion engines the gradual decomposition of the lubrication oils as well as the combustion of fuel lead to the formation of organic and inorganic acids that corrode critical engine parts and surfaces.
Additives

The solution is use of fuel/lube oil additives, generally known as detergents or scavengers. There are numerous types but the ones of interest here are magnesium based additives. The basic scavenging mechanism involves MgO action and can be described as follows:

For cold-end corrosion:

\[ \text{MgO} + \text{SO}_3 \rightarrow \text{MgSO}_4 \]
\[ \text{MgO} + \text{H}_2\text{SO}_4 \rightarrow \text{MgSO}_4 + \text{H}_2\text{O} \]

Which are basically acid neutralization reactions.

For hot corrosion:

\[ \text{MgO} + \text{V}_2\text{O}_5 \rightarrow 3\text{MgO-V}_2\text{O}_5 \]

The magnesium orthovanadate formed has significantly higher melting point than sodium vanadate which means that it has a lower tendency to deposit, it is looser and powdery and easier to remove (e.g. in boiler applications, by using the soot blowers).

Magnesium based additives and detergents can be grouped into the following categories:

i) Oil soluble magnesium organometallic compounds (e.g. sulfonates, carboxylates). These are salts produced by the reaction of MgO or MH with organic acids in a hydrocarbon carrier or solvent. % Mg is less than 6%.

ii) Overbased oil soluble magnesium compounds. The production principle is the same as above, but the MgO or MH is added in excess. These products are not strictly solutions, since they are in fact nano/submicron dispersions of MgO or MgO/MgCO$_3$ in a hydrocarbon carrier. There are many variations that this can be accomplished. MgO or MH are partially reacted with carboxylic/sulfonic acid and/or phenolic surfactants in high boiling hydrocarbons and are subsequently heated above the salt decomposition temperatures. CO$_2$ may also be added to form in-situ MgCO$_3$. % Mg is typically 10-20 %.

iii) Fuel compatible MgO oil dispersions. These are quite different from (i) and (ii) and are basically high % MgO stabilized dispersions in a hydrocarbon carrier. An example formulation is 50% of very fine CCM, 1% emulsifier (e.g. alkanolamide), 4% dispersant (e.g. oleic acid), 2% thickening/stabilizing agent (e.g. alkyl sulfate salt) and balance No.2 fuel oil as carrier. A typical procedure is a) homogenization of emulsifier and dispersant in the carrier, b) addition and mixing of MgO, c) addition and mixing of thickener. Wet milling could possibly be involved to reduce particle size.

iv) MgO/MH water slurries. These can be typical 40-55% stabilized MH slurries or MgO/MH slurries produced by slurrying powder on-site before injection into the system. They
cannot be strictly considered as additives because such slurries will not be miscible with fuel and have to be injected separately into the system.

v) Fine MgO/MH powders. Again, these have to be injected directly into the system.

Requirements

Categories i-ii are produced by dedicated companies using high-end MgO or MH as raw materials for both fuel and lube-oil additives. MgOs are typically synthetic CCMs of medium reactivity with restrictions in CaO (from 0,3 to 1% max) and Na+K depending on the particular additive and the intended use.

Category iii products are again produced by dedicated companies (example Nalco, GRS) while Categories iv-v can be supplied directly by MgO distributors or producers to end-users, most typically as boiler additives in energy plants. Compared to i-ii they will exhibit lower performances. Finely milled natural CCMs (ideally #325 but higher particle sizes may also be acceptable) are possible candidates.

Modes of injection in oil or coal fired boilers

High Temperature corrosion:

Oil soluble compounds and MgO/oil dispersions can be metered directly into the fuel line of oil-fired boilers [see schematic, point (1)] or directly above the burners in coal-fired boilers. Water based slurries or powders can be injected via existing soot blowers (2) with some modifications. Powders can also be fed together with the coal in coal fired boilers (1). Fine particles (i.e. less than 2 μm) can travel all the way towards the cold-end of the boiler, so sufficiently fine materials can help ameliorate both high and cold-end temperature corrosion.

Cold-end corrosion:

Water based slurries or powders can be injected directly in the flue gas stream at a point between the economizer outlet and the combustion air pre-heater (3). The exact point of injection is dependent on many parameters, esp. flue gas temperature and the location of pre-existing ports (e.g., inspection ports).

For slurries and powders, suitable feed equipment is relatively simple, e.g. drum-mounted metering pump and air-aspirated injector for slurries or a powder feeder (with hopper) discharging to a similar aspirator for powders.
Boiler Schematic

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