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Wirkung schwefelbasierter Additive auf Korrosion und Verschmutzung

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Effect of sulphur-based additives on corrosion and fouling

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Introduction

Solid fuels used in power plants often contain minor components that are not at all or barely energetically effective, but which may have an impact on the process as components of the flue gas during the energetic conversion of the fuel (i.e. in the firing and in the downstream process steps, for example the steam generator). These minor components are present in the flue gas in gaseous, liquid, or solid state and phase transitions and reactions take place as the flue gas cools along the flue gas path.

There are different process engineering requirements depending on the type and proportion of these minor components in the fuel. The aim is to ensure that the minor components have as little effect as possible on the stable and intended operation of the main process, i.e. the plant's generation of power. It is thus a question of their influence on availability, operation time and cost and energy efficiency (among other things).

In the case of fossil or biogenic solid fuels, the process can usually be adjusted well, as the properties occur steadily and with little fluctuation. However, in the case of waste and refuse-derived fuels (RDF) with heterogeneous and fluctuating properties, the minor components can have different effects on the process.

The following explanations refer to the requirements in power plants with particularly difficult solid fuels, namely waste, waste wood, and RDF, which are mainly designed as grate firing systems (waste incineration, biomass, and RDF power plants). Almost all industrial products and geogenic substances are possible minor components here. Numerous properties, like fractions and proportions, lumpiness or particle size, compound characteristics (also from an energetic point of view), state of aggregation, phases/species and the behaviour on heating are relevant characteristics and give almost every part of the minor components an individual property. This paper deals with the effects of these minor components regarding fouling and corrosion in the steam generator of waste incineration plants, biomass, and RDF power plants. The portion of the minor components that is transported in the flue gas is of relevance here. The material path to the slag discharge is not included.

Approaches to optimising the combustion process

The effects of the minor components on fouling and corrosion have the potential to significantly influence the overall process in waste incineration, biomass, and RDF power plants. Restriction of availability, shortening of operational time, limitation of energy efficiency (in case of electricity generation) and increase of maintenance expenses are some of the possible effects, wich have a strong economic impact. Consequently, there are extensive efforts in the market to counteract these effects through appropriate process technology.

Suitable measures in this sense are available at different process engineering levels. First, the design features of the firing system and the steam generator can have an influence. In addition, the mode of operation (firing, load fluctuations, etc.) can be adapted, or site-specific technical solutions can be used (e.g. protective coatings, online cleaning).

These process engineering measures to contain the effects of fouling and corrosion act in the firing system and on the heat exchanger surfaces of the steam generator. The chemical composition of the fuel and its minor components should be "controlled" by process engineering in such a way that as few undesired effects as possible occur (e.g. heavy fouling and intensive corrosion).

The effects of these measures can be monitored by probes and sensors [1] to [6].

The heterogeneity and low constancy of the properties of waste fuels also require precise knowledge of the relevant characteristics of the fuel in each case including its minor components, with good temporal resolution (e.g. per grab). In-situ fuel diagnostics [7], [8] and [9] are suitable for this purpose. These are specifically used sensors and probes which enable a kind of "continuous test combustion" when embedded in the main process. These instruments also have a positive effect on the process transparency and the homogeneity of the process properties.

The properties of waste fuels can not only fluctuate but also change significantly on longer time axes. Process engineering measures must adapt accordingly and must also take fouling and corrosion into account. In-situ fuel diagnostics is a suitable tool for this purpose.

In addition to the process-engineering responses to heavy fouling or corrosion, it is possible not only to accept but also to change the chemical composition of the fuel, i.e. to use additives. Basically, there are three possibilities for the introduction of additives: before firing, during firing, or downstream of the firing.

With reference to the causes and mechanisms of fouling growth and the dynamics of corrosion, additives can be used either as a passive dilution of the material conditions or as a reactant (in the flue gas or in the deposits). The spectrum of "useful" substances is broad and ranges from water (vapour) to oxides/silicates, and on to sulphur-based species.

The processes taking place in the flue gas and in the deposits must be understood in order to classify the effectiveness or the mode of action of the additives. The focus of the following explanations is placed on the sulphur-based additives, as these show a positive effect regarding both corrosion and fouling.

Mechanisms of fouling and corrosion

The deposition of flue gas components on heat exchanger surfaces is an essential part of what is called fouling. The reaction of these deposits (and possibly other gaseous components) with the materials of the heat exchangers is termed corrosion. Fouling is therefore both a heat flow impediment, and a cause of steep temperature gradients (and thus high potentials for chemical reactions). Depending on the thickness of the fouling layer and the actual surface temperatures,

specific phases are selectively deposited (cold trap; stickiness). Additionally, the structural properties of the fouling layer (including strength and porosity) change due to mineral reactions. The corrosion products formed during corrosion can also influence the mechanical properties of the layer (sheet-like layers). In addition, the deposits can cause microstructural densification and hardening due to melt formation because of eutectic conditions.

Fouling and corrosion thus show reciprocal imprints. It is therefore not surprising that certain additives help to reduce both fouling and corrosion. Sulphur compounds have the highest relevance regarding this type of effect of additives.

What are the effects of these properties?

Salts form a considerable proportion of the flue gas constituents in waste incineration plants, biomass, or RDF power plants. Different salts precipitate on the given surfaces, with chlorides and sulphates typically having the largest shares (along with hydroxides, phosphates, carbonates, sulphides, etc.). The cations of these salts are dominated by alkaline earth, alkali, and heavy metal elements. Depending on the cation-anion combination, different thermodynamic properties result (e.g. vapour pressure, saturation temperature and melting temperature). The linked selective behaviour patterns of a respective salt is characterised by phase transitions and reactions. All these salts are capable of mixing in any proportions, which also results in eutectic conditions, i.e. the lowering of melting temperatures (in relation to the pure salts). The effect of these properties can lead to strong local enrichment of certain salts.

Regarding the properties of the various relevant salts, it can be summarized that chlorides "bring along" important and conditioning characteristics in the formation of deposits and in corrosion (i.e. they are unfavourable), while sulphates tend not to do so (i.e. they are favourable). It should be noted that mixed salts of chlorides and sulphates can be even more unfavourable than pure chlorides. So, the realm of salts is complex and cannot be clearly divided into black and white or good and bad

The chlorine content in the fuel is a minor component that is typically completely degraded in the original compound (species) in the firing, passes into the gas phase (and thus into the flue gas path), and recombines with other substances. Thus, chlorides or HCl are formed depending on the reaction partners present. HCl typically passes through the boiler as a gas without further reactions. This chlorine species therefore does not participate in the processes of fouling and corrosion.

In a similar way to chlorine, some of the sulphur contained in the fuel is transferred into the gas phase (oxidised) in the firing and either reacts in and after firing to form salts or remains in the flue gas as SO_2 or SO_3. The proportion of SO_2 is usually clearly higher than that of SO_3, for kinetic and thermodynamic reasons. SO_2 behaves in a similar way to HCl (see above) along the flue gas path through the boiler, i.e. it reaches the end of the boiler largely without further reactions. In contrast, SO_3 reacts preferentially with chlorides (referred to as sulphation). Experience from waste incineration, biomass and RDF power plants shows that there are always sufficient chlorides present in the flue gas or on surfaces for all the SO_3 to react with them, i.e. no SO_3 reaches the end of the boiler. Thus, the dew point of sulphuric acid (SO_3 x H_2O) has no relevance in these plants.

This behaviour of SO_3 emphazises the process engineering role of sulphur-based additives.

Function of the sulphur-based additives

The process-engineering task involves "flowing" as much SO_3 as possible around all chlorides as particles (mostly aerosol) in the flue gas, or as deposited particles on heat exchanger surfaces, so that the sulphation reaction takes place. In this way, chloride becomes sulphate,

with the incorporation of SO_3 and the release of HCl (with the participation of water vapour). For example, this sulphation reaction can be shown using a NaCl particle:

$$2\ NaCl\ +\ SO_3\ +\ H_2O\ =\ Na_2SO_4\ +\ 2\ HCl$$

The effect of this process technology can also be described in such a way that the chlorine, which is initially fixed as chloride in and after firing, becomes HCl before it can have a damaging effect on fouling and corrosion. Thus, the - harmless - HCl load in the flue gas increases. Depending on the amount of SO_3 in the flue gas, this sulphation reaction proceeds at different rates [10] but can also be accelerated by additives that contain sulphur. This is particularly helpful in the case of rapid deposit formation, allowing the sulphation reaction to take place before further spillage of the deposits occurs.

Side note: For the dry and semi-dry flue gas cleaning processes, the higher HCl load also brings an improvement in the separation capability of SO_2, since the HCl is needed to provide - as a preliminary reaction - sufficient reactivity (hygroscopic property of calcium chloride) for effective SO_2 separation.

Particularly favourable process characteristics therefore result when the sulphur additive reacts as completely as possible to from SO_3 or decomposes during heating. This is the case for trivalent sulphur salts, such as ammonium sulphate or iron (III) sulphate. Other options are to use "ready" SO_3 gas (formed catalytically outside the boiler) or to oxidise reduced sulphur species (e.g. elemental sulphur) in such a way that a high SO_3/SO_2 ratio is obtained (e.g. using a sulphur burner).

What all these methods of using sulphur-containing additives have in common is that they are specifically designed to increase the SO_3 load and are placed in or after the furnace.

These additives could be dispensed with if the fuel already contained sufficient sulphur and its species led to the highest possible SO_3/SO_2 ratio in the furnace. In such cases the fuel and the furnace would have provided inherent protection against heavy fouling or dynamic corrosion. However, this is usually not the case. Indeed, in recent years many waste fuels have tended to have higher chlorine loads and lower sulphur loads, i.e. exactly the opposite to the optimum. In principle, it is possible to "enrich" the fuel with additional sulphur before firing if corresponding quantities of fuels with a higher sulphur content are available and can be sufficiently mixed, for example in the bunker. Sewage sludge is an example of such a fuel. By contrast, gypsum boards, for example, would be less suitable as the sulphur in this mineral phase (calcium sulphate) is less likely to react to sulphur gases. Whether SO_3 is formed from the sulphur species in the fuel is always a question of fire control. Accordingly, efforts to raise the sulphur level in the fuel usually show a rather diffuse effect in terms of reducing fouling and corrosion. The methods of adding sulphur additives in and after firing described above are usually to be preferred

In principle, the choice of additive should be carefully considered so that the added sulphur compound is also present as SO_3 in the flue gas. In the worst case, only SO_2 is formed from the additive, which not only has no positive effect on corrosion or fouling but increases the amount of operating materials used in the flue gas cleaning system or burdens the capacity of the system.

However, the choice of a suitable additive is only the first step. This still does not clarify in which areas of the steam generator SO_3 is needed for sulphation and in which load it should be present. To circumvent these questions, one could set a high SO_3 load, i.e. a safe excess of SO_3. This is not advisable, as it causes higher costs in the provision of additives and the "surplus" SO_3 also generates additional effort in flue gas cleaning. In addition, the fact that the dew point of the sulphuric acid would be effective in this way and trigger corrosion in the flue gas cleaning area have to be assessed particularly critical.

For good process control of the sulphur additives, it is therefore important to know – at least approximately – the demand for SO_3. It is difficult to acquire this information for several reasons. Firstly, the determination of the SO_3 load in the flue gas is complex because the usual way gas measurements are made – by extracting gas and discharging it from the boiler and analysing it outside of the boiler – is severely limited as particle separation is necessary before the measuring section.

In this way, chlorides are also separated. The flue gas drawn over this filter will lose its SO_3 load to the extent that sulphation of the separated chlorides occurs. Secondly, the sulfation reaction dynamics along the flue gas path is not uniform. If the SO_3 is introduced with the secondary air, for example, then the SO_3 reacts with the chlorides in the 1st pass. Does this leave enough SO_3 for the other radiation passes and for the convective heating surfaces? There is a different distribution along the flue gas path, depending on the species of the chlorides. For example, calcium chloride is preferentially a fouling component in the 1st to the 3rd pass and the heavy metal chlorides preferentially around the heat exchangers in the convective part of the boiler. This must also be considered for the loads and the distribution of the SO_3.

Measurements of the SO_3 load are necessary at any desired location along the flue gas path between the furnace and the flue gas cleaning system to meet these requirements and thus make the process technology of sulphur additives practical and robust. This enables the formulation of a "recipe" for the sulphur additives. This is an individual setting for each fuel (type) and for each furnace.

The sulphation probe as a component of process control

The obstacles for measurement technology with extraction described above can best be overcome if the measurement process takes place directly in the flue gas flow. To do this CheMin has developed a probe that can be used to check the sulphation performance at different locations in the boiler (sulphation probe, Figure 1).
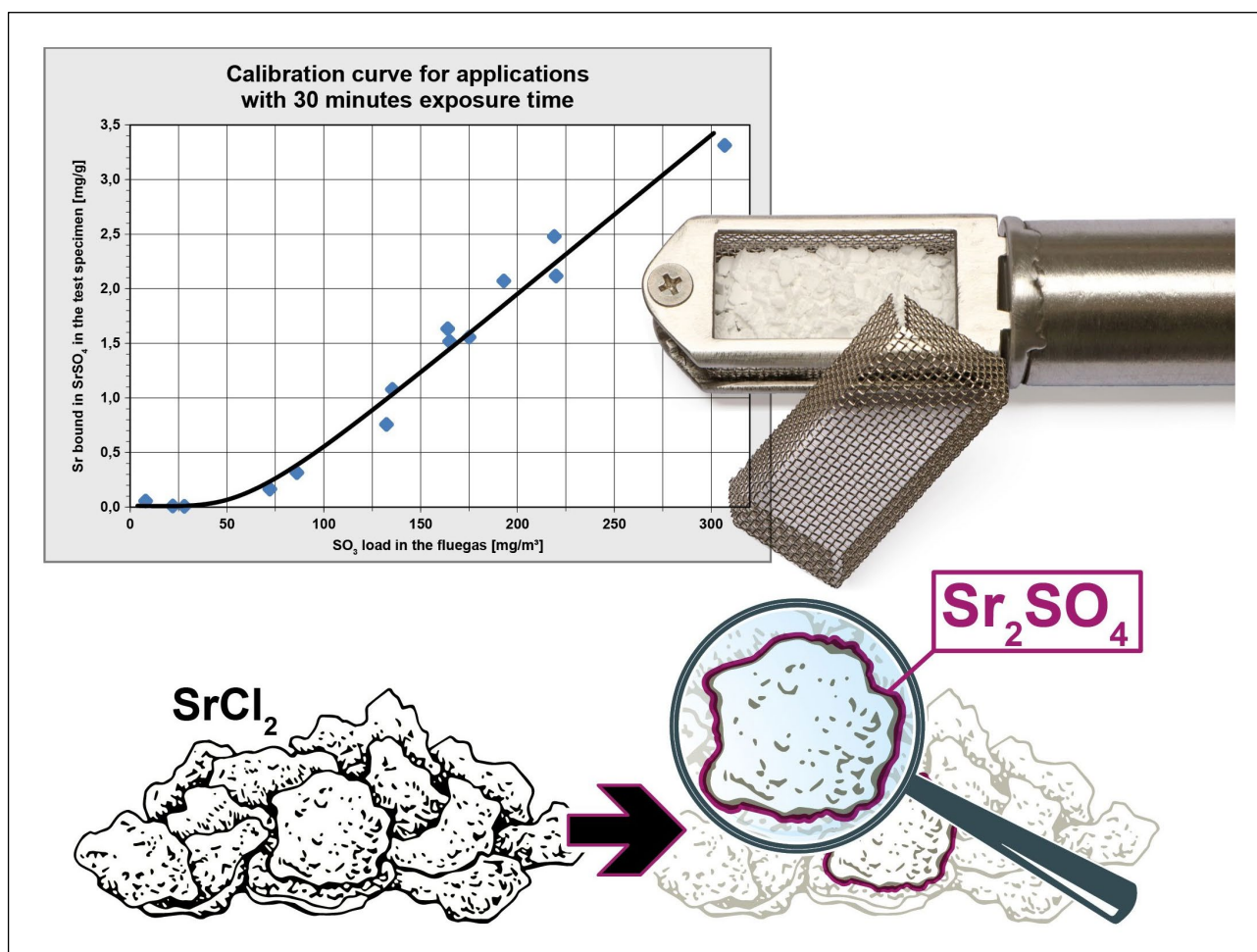
Figure 1: Schematic representation of the sulphation probe including measuring principle.

In this process, a chloride (in the form of a loose bed of flakes) is introduced into the flue gas flow, and removed again after a set time. Any SO_3 present in the flue gas will sulphate the chloride during the exposure time, just as it does on a fouling surface. All other boundary conditions between the probe and the fouling on a heat exchanger surface are the same. Components of the flue gas, for example, will also be deposited on the flakes. Parts of the flakes are thus covered and chlorides, for example, can also be deposited. With a longer probe exposure time these effects increase and the "sole supply" of chloride is overprinted. This limits the exposure time of the probe (positive empirical values are e.g. 30 minutes). The availability of SO_3 can be quantified based on the amount of sulphate to which the offered chloride has reacted. Sulphates can also be among the particles deposited on the flakes. Therefore, it is essential for this measurement technique that it determines only those sulphates that have formed from the chloride flakes. To ensure this, chlorides whose cation typically hardly occurs in waste (and thus also in the flue gas) are used – for example, strontium. The strontium chloride used and the resulting strontium sulphate also offer the advantage that the differences in their solubility allow a simple analytical procedure.

There are many application possibilities for the sulphation probe. A suitable procedure for determining a recipe for the sulphur-containing additive used consists of the following steps:

1. First, the SO_3 load is determined in a "zero run" at several positions along the flue gas path, as shown as an example in Figure 2. This shows at which position which SO_3 load is present in the flue gas with these fuel and firing conditions. The position at the end of the boiler is a control measurement. No SO_3 load should be measured there.
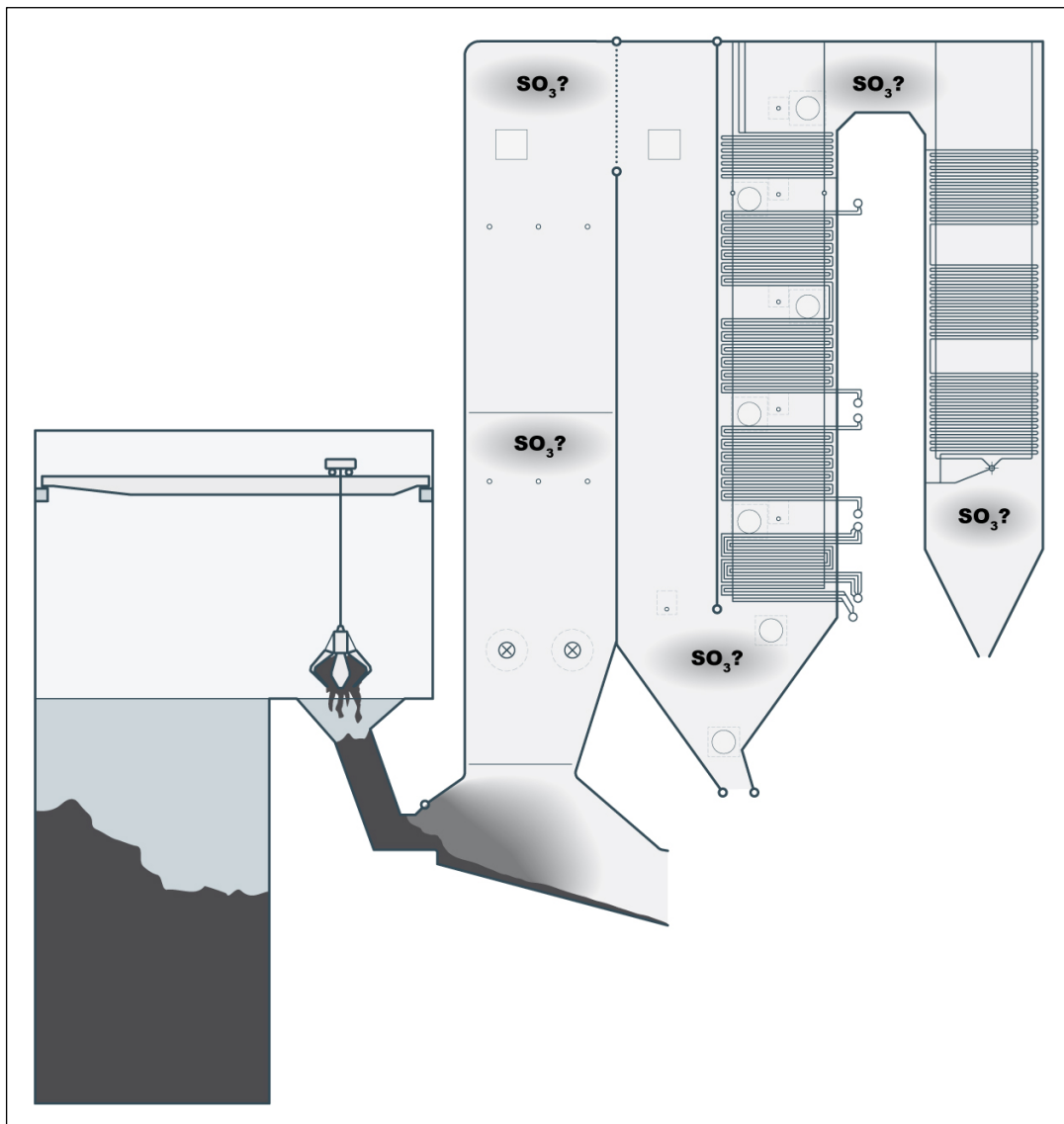
Figure 2: Exemplary implementation of a measurement of the zero state using sulphation probes.

2. Now the sulphur-containing additive is introduced, and the measurements are repeated. Depending on the findings, the amount of additive is then successively increased or decreased and measured again each time. The aim is to detect SO_3 at all positions where there are high corrosion dynamics or strong deposit growth and to find no SO_3 at the end of the boiler.

3. These measurements are repeated several times in the course of an operation period. The reason for this procedure is that slagging in the furnace and basic fouling of all heat exchanger surfaces changes the temperature distribution along the flue gas path and thus also the distribution of the salts.

4. A check of the recipe found should be carried out as soon as relevant boundary conditions change in the longer term, e.g. the load or the fuel mix.

Different injection positions are possible depending on the type of sulphur additive. Injection at several positions along the flue gas path is also conceivable. For each injection position, it is important to achieve the most homogeneous distribution of SO_3 possible across the flue gas cross-section. Whether this is successful can also be determined with the sulphation probe (application on different sides or different immersion depths).

The use of temperature-range probes (see above) at the relevant positions in the boiler is a supplement to checking the effectiveness of the additive injection concerning fouling and corrosion.

Conclusion and outlook

Both fouling and corrosion can be significantly reduced by well-chosen and well-adjusted process technology of sulphur-containing additive. This is currently a particularly relevant option, as the shortage of raw materials is negatively affecting their availability and their cost.

Lower corrosion dynamics also provide options for increasing energy efficiency (higher superheater temperature) and better availability (fewer unplanned shutdowns). These are also currently important measures for domestically based energy supply. With less pollution, it may be possible to extend operation periods and thus increase availability.

All these effects also reduce maintenance costs. Introducing the process technology of injecting sulphur-containing additives will usually pay for itself in the short term, if used correctly.

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