

TMT 15[®] - Facts for the use in flue gas scrub water

Application information / Info 16 E

1. What is TMT 15[®]?

TMT 15[®] is a 15 % aqueous solution of Trimercapto-s-triazine, trisodium salt (C₃N₃S₃Na₃, CAS-RN 17766-26-6). It is primarily used to precipitate heavy metals. The chemical characteristics of TMT 15[®] are not comparable to other triazine compounds, e. g. those used as active ingredients in herbicides.

2. Who produces TMT 15[®]?

Since 1979, TMT 15[®] has been exclusively manufactured by Evonik Degussa GmbH. TMT 15[®] can be ordered directly or through authorised distributors in one-way or multi-way containers.

3. What is TMT 15[®] used for?

TMT 15[®] is used to precipitate single and bivalent heavy metals such as Ag, Cd, Cu, Hg, Ni and Pb from waste water streams. If the effluent, however, contains heavy metal complexes which can not be eliminated as hydroxides due to neutralisation, TMT 15[®] can be used for precipitation.

4. Where is TMT 15[®] used?

In particular, TMT 15[®] has shown high efficiency in the treatment of effluents/waste water from metal working-, chemical-, photographic- or mining industry and especially from thermal processes (municipal-, hazardous waste, sludge incinerators and power plants). For the time being TMT 15[®] is used in several hundred incineration plants on commercial basis, predominantly for the precipitation of mercury.

5. How is a typical flue gas treatment system operated?

Passing a scrubbing system the heavy metals from the flue gas are transferred into the scrubbing water. As a rule, the concentration of heavy metals in the scrubbing water exceeds the allowed discharge limit and as a consequence have to be eliminated. For the first step the acid scrubbing water is neutralised with lime [(Ca(OH)₂] or caustic soda [NaOH]. During this step most of the heavy metals are almost precipitated as hydroxides. However, especially mercury [Hg] is only partially removed, as it forms in the presence of chlorides in high concentrations, a soluble and very stable mercury-tetrachloro-complex [(Hg(Cl₄)²⁻). As a consequence other technologies for its removal are required.

Neutralisation combined with TMT 15[®] is an effective process for separating mercury. Neutralisation followed by TMT 15[®] dosing yields a precipitate consisting of metal hydroxides and metal-TMT compounds. Most of the heavy metals are removed by the lime or caustic soda, where as the remaining metal complexes - especially Hg - are precipitated by TMT 15[®].

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6. What is the most favourable way to use TMT 15[®]?

The previously described combination of neutralisation and TMT 15[®] dosing is the approved standard method to treat flue gas scrubbing water.

As a rule the TMT 15[®] dosage rate to the scrub water is calculated based on the mercury content; under normal operational conditions where the Hg-concentration is kept within limits, a TMT 15[®] addition is not necessary. Whether TMT 15[®] is required in power plants is depending e. g. upon the quality of coal.

For ecological and economic reasons the TMT 15[®] quantity should be optimised. For example an adjustment of the TMT 15[®] amount is possible by using an on-line mercury analyzer. This combination is mainly of interest for incinerators where the mercury concentration in the waste water varies considerably.

7. How stable are Heavy Metal-TMT compounds?

The leachability of heavy metal-TMT compounds from flue gas scrubbing water has been tested according to the German Standard DIN 38 414, part 4 (at pH 4) and the Swiss Standard TVA draft 8/88. The results show that heavy metal-TMT compounds, especially TMT-mercury, are transferred into hardly leachable compounds.

The complete cracking of Mercury-TMT is only possible with aqua regia under heat and pressure (4 h 180 °C). This is not achievable with concentrated nitric or sulphuric acid.

Mercury-TMT precipitates are thermally stable up to 250 °C. This allows subsequent drying processes. Due to the high thermal stability of Mercury-TMT (< 250 °C) TMT 15[®] is also recommended for the mercury precipitation in flue gas scrubbing water with connected drying processes at the outlet side.

8. How can an excess of TMT 15[®] be analysed?

TMT 15[®], as such in aqueous solutions can be determined by UV-spectroscopy to the single digit ppm range.

9. What happens when there is an excess of TMT 15[®]?

The dosage rate of TMT 15[®] is calculated on the basis of the maximum quantity of Hg which is expected. Based on our experience, about 50 ml of TMT 15[®] per cubic meter of flue gas scrubbing water can be taken on an average, which means that this quantity can precipitate up to 6 g Hg/m³.

Other heavy metals which are usually present in much higher concentrations (in municipal waste incinerators hundreds of grams per cubic meter) are already precipitated as hydroxides during the neutralisation step. Since the solubility product of heavy metal-TMT compounds is much lower than the corresponding hydroxides, the excess of TMT 15[®] reacts with the hydroxides, (the solubility products for Cd(OH)₂ and Cd₃TMT₂ are ≈ 10⁻¹⁴ and ≈ 10⁻³³ respectively) by forming hardly soluble heavy metal-TMT-compounds.

The conversion of hydroxides to heavy metal-TMT precipitates proceeds until the excess of TMT 15[®] is used up. This phenomenon has been observed many times under practical applications. A TMT 15[®] excess in this application is selfregulating.

TMT 15[®] will be adsorbed on activated sludge.

10. What are the alternatives to TMT 15[®]?

Besides TMT 15[®], sodium sulphide, dithiocarbamate, and sodium trithiocarbonate are commercially available precipitating agents.

11. What favours TMT 15[®]?

TMT 15[®] has very favourable toxicological and ecological properties compared to all other precipitating agents. Besides the very low acute toxicity (LD₅₀ 7878 mg TMT 15[®]/kg *) TMT 15[®] is practically not toxic for fishes (LC₅₀ 13720 mg TMT 15[®]/l *) and water fleas (Daphnia magna, EC₅₀ 4224 mg TMT 15[®]/l *). TMT 15[®] is not mutagen and shows no acute toxicity against bacterial population. The toxicity to green algae is low (IC₅₀ 273 mg TMT 15[®]/l *).

Because of the irritative effect to the eyes TMT 15[®] is labelled with the hazard statement "H319 - causes serious eye irritation".

TMT 15[®] has a good storage stability and is not considered as a dangerous substance according to the transport regulations. TMT 15[®] is a safe product to handle. Should TMT 15[®] come into accidental contact with acids only minor amounts of hydrogen sulphide and no carbon disulphide are released and the acidic form of TMT 15[®] (TMT-H₃) would precipitate, that is practically insoluble in water. This reaction is reversible and the TMT sodium salt can be achieved again by the addition of caustic soda.

As TMT 15[®] is stable in the acidic range, TMT 15[®] is directly added to the acidic scrubber water for the Hg-precipitation in some plants. The acid/base reaction of TMT is used to determine the TMT 15[®] concentration.

TMT 15[®] is not a dangerous substance within the meaning of transport regulations.

* *Data calculated for the commercial product TMT 15[®].*

12. Are there fields of application for TMT 15[®] for the reduction of mercury emissions in flue gas?

In addition to the proved application of TMT 15[®] in scrubbing water from flue gas treatment TMT 15[®] can also be used directly in the alkaline scrubbers of garbage incineration plants to reduce the emission of mercury in the clean gas. Mercury is precipitated in the scrubbing water. The TMT-mercury-compound is hardly soluble and resistant against temperatures up to 200°C and as a consequence a reduction to the slight volatile metallic mercury is inhibited.

The precipitated TMT-mercury-compound can either be separated in the waste water treatment plant, or in the spray-dryer of the combustion plant.

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