ON16 COMPOSITION

Mineralogical Analysis *(DRX)*

Components	Formula
Goethite	FeOOH
Hematites	α-Fe_2O_3
Mica-group minerals	$(K,Na)(Al,Mg,Fe)_2$ $[(Si,Al)_4O_{10}](OH)_2$
Quartz	α-SiO_2
Other	Amorphous

FeOOH / α-Fe_2O_3 → These are the only components able to H_2S removal

Mica-group minerals / α-SiO_2 → These are impurities associated to natural source

Amorphous → Mainly water and non-crystalline components

ON16 REMOVAL REACTION

The reactivity of iron oxides with H2S has been well known for many years. In fact, iron oxide wood chips (iron sponge), which are widely used in the USA for external upgrading of biogas, were one of the first H_2S removal systems developed in the early 20th century.

The main difference between Micronox ON16 and an iron sponge (or iron oxide pellet) is that reaction takes place inside the digester instead of externally. This prevents H_2S from coming out of solution from the water substrate, decreasing the impact of H_2S on the vessel and tubes.

ON16 reactions between FeOOH/Fe_2O_3 and H_2S are shown in Figure 1, while Figures 2 and 3 show extracts from different publications.

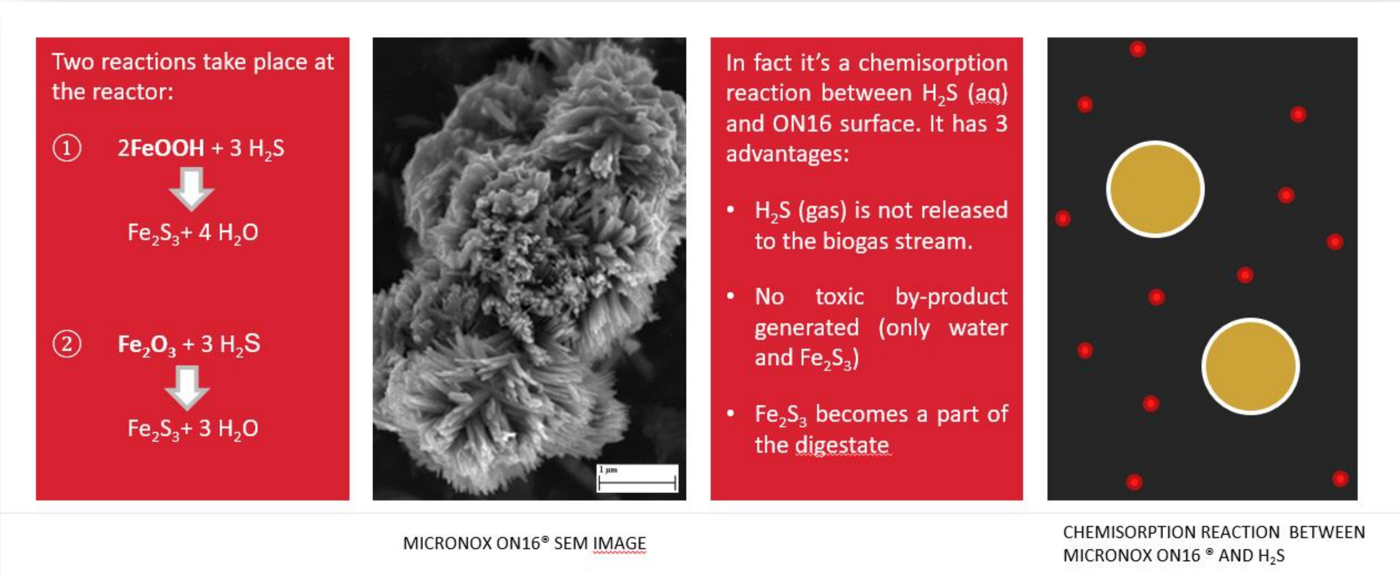

Figure 1

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2 In-situ (digester) sulfide abatement by addition of iron salts/oxides to the digester slurry

Iron chlorides, phosphates or oxides are directly added into the digester slurry or into the feed substrate in a pre-storage tank. The addition of $FeCl_2$, which is a liquid, is the most regularly practiced. Iron hydroxide ($Fe(OH)_3$ or $Fe(OH)_2$) in solid form and ferrous chloride ($FeCl_3$) can also be added. They react then with the produced hydrogen sulfide and form insoluble iron sulfide salts. Due to this precipitation stripping of H_2S into the biogas is prevented.

Ferrous chloride:	$Fe^{+2} + S^{-2} \rightarrow FeS$	Eq. 1
Ferrous hydroxide:	$2Fe(OH)_3 + H_2S \rightarrow 2Fe(OH)_2 + S + 2H_2O$ $Fe(OH)_2 + H_2S \rightarrow FeS + 2H_2O$	Eq. 2
Ferric chloride:	$2FeCl_3 + 3H_2S \rightarrow 2FeS\downarrow + S\downarrow + 6HCl$	Eq. 3

Figure 2

3.0 APPROACH - BABCOCK AND WILCOX

The approach taken by Babcock and Wilcox is to remove H_2S from the make-gas by reaction with iron oxide at a comparatively high temperature. The objective is to minimize the amount of cooling needed between the gasifier and the second stage combustion device.

The use of iron oxide to remove H_2S is not a new or unique approach. Historically hydrated iron oxide has been used for decades in oxide boxes to remove H_2S from coke oven gas. At the present time, work is being done by the Bureau of Mines on a concept that removes H_2S with a sintered material made from iron oxide and fly ash. Our concept is different in as much that we start out with carbon steel and generate, on the surface of the carbon steel, an FeOx scale that is used as the desulfurization agent. In terms of the mechanism of sulfur removal, it is likely that both the Bureau of Mines' and our concepts are alike.

Briefly, the concept removes H_2S by:

(1) Fe/FeOx + H_2S (sour gas) $\longrightarrow$ FeSx + H_2O (sweet gas)

Figure 3

EFFECTS OF ON16 ON ANAEROBIC REACTION BY-PRODUCTS

Micronox ON16 is a solid mineral, not a salt, so powder is not dissolved inside the reactor, but just dispersed. As it is micronized, and has a density similar to water, it remains dispersed in the medium as long as there exists agitation. As substrate leaves the system, the depleted ON16 will also leave. The colour of the final product changes from yellowish brown to reddish brown/black due to the reaction.

ON16 concentration in final substrate depends on the dosage, and thus on the initial and target H_2S concentration. Table below shows three examples to calculate final ON16 concentration in the exhausted digestate.

	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3
TYPE OF PRODUCT	Sludges WTTP	Urban Organic Waste	Dairy
DAILY SUBSTRATE (tn/day)	35	240	234
BIOGAS FLOW (m^3/day)	12000	19000	3200
H_2S INITIAL (ppm)	4000	2500	2000
H_2S TARGET (ppm)	200	500	800
DAILY ON16 ADITION (kg)	200	350	40
% ON16 OVER DAILY SUBSTRATE OUTLET	**0,57%**	**0,15%**	**0,02%**

These real examples of ON16 application are quite different, not only for the substrate type, but also for the biogas flow and H_2S concentration. In any case, we can see that ON16 concentration in substrate outlet, assuming that the output is equal to the input material, is always under 1%. Concentration will be higher if solid waste is separated from water in a further step, as ON16 would mainly remain in the solid phase.

In addition to iron (Fe) and sulphur (S), ON16 would also add to final digestate other micronutrients such as Aluminium (Al), Sodium (Na), Silicon (Si), Magnesium (Mg), Manganese (Mn), Potassium (K) or Calcium (Ca).

According to researchers more than 17 nutrients are essential for plants:

- Carbon(C), Hydrogen(H) and Oxygen(O) naturally available and not supplied to plants.
- Nitrogen(N), Phosphorous(P) and **Potassium(K)** called major nutrients required in larger quantities by plants and need to be supplied time to time.
- **Calcium(Ca), Magnesium(Mg) and Sulphur(S)** required in little fewer quantities than major nutrients and called as secondary nutrients.
- Micronutriens are required in very small quantities by plants and they have very vital roles in the physiology of the plants. These micronutrients are Zinc (Zn), Boron (Bo), **Iron (Fe), Manganese (Mn)**, Copper (Cu), Molybdenum (Mo), **Silicon (Si)**, Nickel (Ni), Cobalt (Co) and **Sodium (Na)**. The micronutrients in plants have an active role in flower initiations, fertilization, fruit setting and disease resistant ability.

To sum up:

- ON16 is a natural mineral that can be easily added to the reaction vessel for an in-situ removal of H_2S during biogas production.
- The main components are iron oxide, iron oxy-hydroxide, mica components and quartz. Final products after the reaction with H_2S are Fe_2S_3, S (elemental) and water.
- 8 of the most important secondary nutrients and micronutrients for plants are present in our natural source for ON16. Therefore, although concentration is not so high in the depleted substrate, it is an interesting additional source of elements for fertilizer.

Dune Prat
R&D Manager