



SwissBiogas.com

Additives for Results-Driven Anaerobic Digesters

Autark Investments and Projects AG
Dept. SwissBiogas.com
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Switzerland

www.swissbiogas.com



SwissBiogas.com presents:
SBGx desulphurisation and gas booster additive



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Desulphurisation, why?

- Protects the CHP unit
- Protects the engines
- Raises the efficiency of the whole plant
- Lowers the operating costs
- Increases the operational safety



Current desulphurisation methods:

- No reactor intervention
- Air injection
- Addition of
 - Ferrous / Ferric oxide: FeO / Fe_2O_3
 - Iron oxide-hydroxide: $\text{FeO}(\text{OH})$
 - Ferrous / Ferric chloride: FeCl_2 / FeCl_3



Air injection, why not:

- Impairs fermentation and methane generation (Hinge 2014)
- Atmospheric nitrogen is unnecessarily added to the biogas (Ammonia)
- Excessive introduction of oxygen leads to formation of corrosive sulfuric acid:
 $2\text{O}_2 + \text{H}_2\text{S} \rightarrow \text{H}_2\text{SO}_4$ instead of $\text{O}_2 + 2\text{H}_2\text{S} \rightarrow 2\text{S}\downarrow + 2\text{H}_2\text{O}$ [1], [2]
- % O_2 higher than 0.9% before CHP has a negative effect on efficiency of CHP
- Sulfur deposits formed in the fermenter gas compartment break off from time to time and drop back into the fermenter liquid
- Risk of explosion
- The air flow must be controlled and adapted regularly:
 - a) Less gas production but same air injection results in too much O_2 and dilution
 - b) Higher gas production with same air injection results in too less O_2 with weak desulphurisation effect

Ferrous / Ferric chloride, why not:

- Reduces volume of produced biogas (12% - 32%)
(Dentel 1982, Johnson 2003, Smith 2008, 2009, Dauknys 2011)
- Releases chlorides during desulphurisation → More corrosive than H₂S
- Forms HCl which penetrates the bacterial membrane
- Classified as dangerous substance
- Considered a corrosive substance
- $\text{FeCl}_2 + \text{H}_2\text{S} \rightarrow \text{FeS}\downarrow + 2\text{HCl}$
- $2\text{FeCl}_3 + 3\text{H}_2\text{S} \rightarrow 2\text{FeS}\downarrow + \text{S}\downarrow + 6\text{HCl}$

CORROSIVE



IRRITANT





Iron oxide-hydroxide, why not:

- **Iron oxide-hydroxide binds metals.**

These materials are known to bind a wide range of other compounds from water, including trace metals, arsenic, selenium, silicate, and organics. Metals such as manganese, cobalt, nickel, and zinc are known to bind to iron oxide hydroxide in simulated seawater solutions. It has also been claimed that the binding of copper and zinc by natural iron oxide-hydroxide sediments exerts a powerful control on the concentration of copper and zinc in polluted rivers and estuaries. Although not studied in seawater, it has also been observed that phosphate binding by iron oxide-hydroxide actually increases its binding of copper, cadmium, and nickel in freshwater.

- Reference : <http://www.reefkeeping.com/issues/2004-11/rhf/>

Ferrous / Ferric oxide, why yes:

- Measurably reduces struvite formation
- Lowers H₂S very effectively
- Increases methane production
- Prevents corrosion of plant and CHP
- Reduces HRT
- Chemical equations:
 - Ferrous oxide: $\text{FeO} + \text{H}_2\text{S} \rightarrow \text{FeS}\downarrow + \text{H}_2\text{O}$
 - Ferric oxide: $\text{Fe}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow 2\text{FeS}\downarrow + \text{S}\downarrow + 3\text{H}_2\text{O}$

Sources: [1] $\text{Fe}^{2+} + \text{S}^{2-} \rightarrow \text{FeS}\downarrow$

[2] $2\text{Fe}^{3+} + 3\text{S}^{2-} \rightarrow 2\text{Fe}^{2+} + 2\text{S}^{2-} + \text{S}\downarrow \rightarrow 2\text{FeS}\downarrow + \text{S}\downarrow$

Comparison of desulphurisation methods, SBGx by SwissBiogas.com against others:

	<i>SBGx</i>	<i>Iron Oxide</i>	<i>Iron Oxide-Hydroxide</i>	<i>Iron Chloride</i>	<i>Air Injection</i>
<i>Investment into</i>					
Storage and Handling	outside, low	covered, low	covered, low	covered, high	not applicable
Dosing Equipment	none / low	none / low	medium	medium	high
<i>Risk of / to</i>					
Exposure / Personnel	low	low	low	high	n. a.
Explosion	low	low	low	low	high
Corrosion	low	low	low	high, HCl ^A	high, H ₂ SO ₄ ^B
Gas Impurities	low	low	low	low	high
Reaction Products	none	none	none	HCl	H ₂ SO ₄
<i>Other Characteristics</i>					
Chemical Composition	FeO and Fe ₂ O ₃ ^C	Fe ₂ O ₃	FeO(OH)	FeCl ₂ or FeCl ₃	n. a.
Reactive Iron Ion Content	> 60% ^D	30% - 60%	10% - 15%	10% - 14%	n. a.
Reaction Speed	high	low	low	high	low
Deposit / Buffer Effect	high	high	medium	none	none
Effect on Bacterial Health	positive	normal	normal	negative	negative
Effect on Gas Yield	positive	normal	normal	0 to minus 32% ^E	negative
Trace Element Addition	recommended	required	required	required	required
Shelf Life	> 12 months	> 12 months	< 12 months	< 12 months	n. a.
Price per chem. Reaction	medium	high	medium	high	n. a.

^A IUPAC: Hydrogen chloride or Hydrochloric acid gas

^B IUPAC: Sulfuric acid

^C See www.swissbiogas.com/Resources - Download Area/Effects of Different States of Fe on Anaerobic Digestion: A Review

^D Analysis June 2022

^E See www.swissbiogas.com/Resources - Download Area/The effect of iron salt on anaerobic digestion and phosphate release to sludge liquor

Calculation of the Reactive Iron Ion Content (RIIC)

The most significant and differentiating factor of any Fe-based additive is its Reactive Iron Ion Content (RIIC; Higher = Better). RIIC is a metric, introduced and used by SwissBiogas.com, to reliably project the potential of additives to bind sulfur and to support the growth of methanogens. Based on the RIICs of its respective iron compounds, the RIIC of any additive can be calculated as follows:

- $\text{RIIC}(\text{FeO}) = 0.7773 \rightarrow \text{RIIC}(\text{FeO additive}) = \text{Content FeO [\%]} \times 0.7773$
- $\text{RIIC}(\text{Fe}_2\text{O}_3) = 0.6994 \rightarrow \text{RIIC}(\text{Fe}_2\text{O}_3 \text{ additive}) = \text{Content Fe}_2\text{O}_3 [\%] \times 0.6994$
- $\text{RIIC}(\text{Fe}_3\text{O}_4) = 0.7236 \rightarrow \text{RIIC}(\text{Fe}_3\text{O}_4 \text{ additive}) = \text{Content Fe}_3\text{O}_4 [\%] \times 0.7236$
- $\text{RIIC}(\text{FeCl}_2) = 0.4406 \rightarrow \text{RIIC}(\text{FeCl}_2 \text{ additive}) = \text{Content FeCl}_2 [\%] \times 0.4406$
- $\text{RIIC}(\text{FeCl}_3) = 0.3443 \rightarrow \text{RIIC}(\text{FeCl}_3 \text{ additive}) = \text{Content FeCl}_3 [\%] \times 0.3443$
- $\text{RIIC}(\text{FeO}(\text{OH})) = 0.6285 \rightarrow \text{RIIC}(\text{FeO}(\text{OH}) \text{ additive}) = \text{Content FeO}(\text{OH}) [\%] \times 0.6285$
- $\text{RIIC}(\text{Fe}(\text{OH})_2) = 0.6215 \rightarrow \text{RIIC}(\text{Fe}(\text{OH})_2 \text{ additive}) = \text{Content Fe}(\text{OH})_2 [\%] \times 0.6215$
- $\text{RIIC}(\text{Fe}(\text{OH})_3) = 0.5226 \rightarrow \text{RIIC}(\text{Fe}(\text{OH})_3 \text{ additive}) = \text{Content Fe}(\text{OH})_3 [\%] \times 0.5226$
- $\text{RIIC}(\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}) = 0.5226 \rightarrow \text{RIIC}(\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} \text{ additive}) = \text{Content Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} [\%] \times 0.5226$

Examples:

1. Additive X: 60% FeO $\rightarrow \text{RIIC}(\text{Additive X}) = 60\% \times 0.7773 = 46.6\%$
2. Additive Y: 40% FeCl₃ $\rightarrow \text{RIIC}(\text{Additive Y}) = 40\% \times 0.3443 = 13.8\%$
3. Additive Z: 10% FeO + 20% Fe₂O₃ + 45% FeO(OH)
 $\rightarrow \text{RIIC}(\text{Additive Z}) = 10\% \times 0.7773 + 20\% \times 0.6994 + 45\% \times 0.6285 = 50.0\%$

Remark: RIIC(SBGx) > 60% (Analysis June 2022)

Comparison table of chemical equations with different iron based additives:

<i>Desulphurisation agent</i>		<i>RIIIC [%]</i>	<i>Chemical equation</i>	
Iron(II) oxide	SBGx	77.73	FeO	+ H ₂ S → FeS ↓ + H ₂ O
Iron(III) oxide	SBGx	69.94	Fe ₂ O ₃	+ 3H ₂ S → 2FeS ↓ + S ↓ + 3H ₂ O
Iron(II,III) oxide		72.36	Fe ₃ O ₄	+ 4H ₂ S → 3FeS ↓ + S ↓ + 4H ₂ O
Iron(II) chloride		44.06	FeCl ₂	+ H ₂ S → FeS ↓ + 2HCl ^A
Iron(III) chloride		34.43	2FeCl ₃	+ 3H ₂ S → 2FeS ↓ + S ↓ + 6HCl
Iron(III) oxide-hydroxide		62.85	2FeO(OH)	+ 3H ₂ S → 2FeS ↓ + S ↓ + 4H ₂ O
Iron(II) hydroxide		62.15	Fe(OH) ₂	+ H ₂ S → FeS ↓ + 2H ₂ O
Iron(III) hydroxide		52.26	2Fe(OH) ₃	+ 3H ₂ S → 2FeS ↓ + S ↓ + 6H ₂ O
Iron(III) oxide trihydrate		52.26	Fe ₂ O ₃ ·3H ₂ O	+ 3H ₂ S → 2FeS ↓ + S ↓ + 6H ₂ O

Also worth listing: Biological desulphurisation

O ₂ addition dosed correctly	O ₂	+ 2H ₂ S →	2S ↓ + 2H ₂ O
O ₂ addition overdosed	2O ₂	+ H ₂ S →	H₂SO₄ ^B

^A IUPAC: Hydrogen chloride or Hydrochloric acid gas

^B IUPAC: Sulfuric acid

Sources: - https://tu-dresden.de/ing/maschinenwesen/ifvu/ressourcen/dateien/tvu/forschungsprojekte/forschung_alt/entschwefelungsverfahren/bge_in_landw_anlagen.pdf?lang=en
 - <http://www.scielo.org.za/pdf/wsa/v44n2/04.pdf>



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The components of SBGx as base before individual adjustments to customers' requirements

Note: The industry-leading high reactive iron ion content (RIIC) > 60%

<i>SBGx</i>	<i>[%]</i>
FeO	> 35.0
Fe ₂ O ₃	> 35.0
MnO	< 1.0
CaO	< 0.5
Al ₂ O ₃	< 0.5
MgO	< 0.5
Cr ₂ O ₃	< 0.2
Zn	< 0.1
Cu	< 0.1
NiO	< 0.1
K ₂ O	< 0.05
CoO	< 0.05

Analysis June 2022



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How we pack and ship:

Delivered in powder form in

- 20 kg bags or as per
- individual requirements

Please contact your agent for availability.

