SwissBiogas.com
Additives for Results-Driven Anaerobic Digesters

Autark Investments and Projects AG
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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

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Common desulphurisation methods:

- Filters, no reactor intervention
- Air injection
- Use of one or a combination of the most commonly used additives:
  - Iron(II) / (III) / (II,III) oxide: FeO / Fe_2O_3 / Fe_3O_4
  - Iron(II) / (III) chloride: $FeCl_2$ / $FeCl_3$
  - Iron(III) oxide-hydroxide: $FeO(OH)$
  - Iron(II) / (III) hydroxide: $Fe(OH)_2$ / $Fe(OH)_3$
  - Iron(III) oxide trihydrate: $Fe_2O_3 \cdot 3H_2O$

  Note: Iron(II) = Ferrous; Iron(III) = Ferric

- For each of the additives and their combinations listed above, SBG's *RIIC calculator* can evaluate the respective *reactive iron ion content* plus *H2S reduction ratio* and compare them with that of SBGx.

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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 sulphuric acid:
  $2O_2 + H_2S \rightarrow H_2SO_4$ instead of $O_2 + 2H_2S \rightarrow 2S\downarrow + 2H_2O$ [1], [2]
- % O_2 higher than 0.9% before CHP has a negative effect on efficiency of CHP
- Sulphur 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

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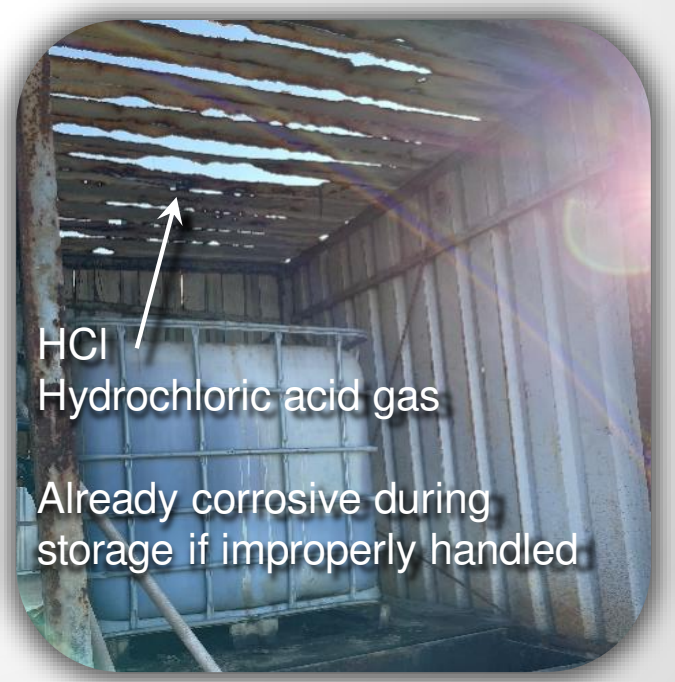
Iron(II)/(III) chloride, why not:

- Reduces volume of produced biogas (12% - 32%)
  (Dentel 1982, Johnson 2003, Smith 2008, 2009, Dauknys 2011)
- Releases chlorides during desulphurisation → More corrosive than H_2S
- Forms hydrogen chloride which penetrates the bacterial membrane
- Classified as dangerous substance
- Considered a corrosive substance
- $FeCl_2 + H_2S \rightarrow FeS\downarrow + 2HCl$
- $2FeCl_3 + 3H_2S \rightarrow 2FeS\downarrow + S\downarrow + 6HCl$

CORROSIVE

IRRITANT



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Iron(III) 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.

- Source: http://www.reefkeeping.com/issues/2004-11/rhf/

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Side note: Iron(II) sulphate ("Grünsalz"), why not:

- **Wikipedia (DE):** "Eisen(II)-sulfat (auch Ferrosulfat, *Grünsalz*, ..."

- **Iron fertiliser hazards**
  According to the [German] ARD magazine, iron fertiliser is recommended in many specialist shops as a remedy against moss in the lawn. However, they do not mention the sometimes serious side effects and other dangers of the fertiliser. This is because iron fertiliser contains the *highly toxic active ingredient iron(II) sulphate [$FeSO_4$]*. When it comes into contact with water or other liquids, it produces gases or sulphuric acid, which can irritate the skin, eyes and respiratory tract. In the worst case, the sulphuric acid has a corrosive effect on the skin. Because of these dangers, the packaging of the iron fertiliser also points out the *need for appropriate protective clothing*.

- Source, in German: https://www.t-online.de/heim-garten/garten/id_58200876/gefahren-beim-umgang-mit-eisenduenger.html

- $FeSO_4 + H_2S \rightarrow FeS\downarrow + H_2SO_4$ or $FeSO_4 + H_2O \rightarrow FeO + H_2SO_4$ See article above.

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Iron(II)/(III) oxide, why yes:

- Measurably reduces struvite formation
- Lowers H_2S very effectively
- Increases methane production
- Prevents corrosion of plant and CHP
- Reduces HRT
- Chemical equations:
  - Ferrous oxide: $FeO + H_2S \rightarrow FeS\downarrow + H_2O$
  - Ferric oxide: $Fe_2O_3 + 3H_2S \rightarrow 2FeS\downarrow + S\downarrow + 3H_2O$

Sources: [1] $Fe^{2+} + S^{2-} \rightarrow FeS\downarrow$
[2] $2Fe^{3+} + 3S^{2-} \rightarrow 2Fe^{2+} + 2S^{2-} + S\downarrow \rightarrow 2FeS\downarrow + S\downarrow$

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

v1.14	*SBGx*	*Iron Oxide*	*Iron Oxide-Hydroxide*	*Iron Chloride*	*Air Injection*
Investment into					
Storage and Handling	outside, low	covered, low	covered, low	covered, high	not applicable
Dosing Equipment	none / low	none / low	medium	medium	high
Risk of / to					
Exposure / Personnel	low	low	low	high	n. a.
Explosion	low	low	low	low	high
Corrosion	low	low	low	high, HCl [A]	high, H_2SO_4 [B]
Gas Impurities	low	low	low	low	high
Reaction Products	none	none	none	HCl	H_2SO_4
Other Characteristics					
Chemical Composition	FeO and Fe_2O_3 [C]	Fe_2O_3	FeO(OH)	$FeCl_2$ or $FeCl_3$	n. a.
Reactive Iron Ion Content	> 60% [D]	30% - 60%	15% - 30%	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.

Anecdotally, *highly toxic* iron(II) sulphate, aka "Grünsalz" in German, can also be used as an additive: $FeSO_4 + H_2S \rightarrow FeS\downarrow + H_2SO_4$

[A] IUPAC: Hydrogen chloride, other name: 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 March 2023
[E] See *www.swissbiogas.com/Resources - Download Area/The effect of iron salt on anaerobic digestion and phosphate release to sludge liquor*

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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:

- RIIC(FeO) = *0.7773* → RIIC(FeO additive) = Content FeO [%] x *0.7773*
- RIIC(Fe_2O_3) = *0.6994* → RIIC(Fe_2O_3 additive) = Content Fe_2O_3 [%] x *0.6994*
- RIIC(Fe_3O_4) = *0.7236* → RIIC(Fe_3O_4 additive) = Content Fe_3O_4 [%] x *0.7236*
- RIIC($FeCl_2$) = *0.4406* → RIIC($FeCl_2$ additive) = Content $FeCl_2$ [%] x *0.4406*
- RIIC($FeCl_3$) = *0.3443* → RIIC($FeCl_3$ additive) = Content $FeCl_3$ [%] x *0.3443*
- RIIC(FeO(OH)) = *0.6285* → RIIC(FeO(OH) additive) = Content FeO(OH) [%] x *0.6285*
- RIIC($Fe(OH)_2$) = *0.6215* → RIIC($Fe(OH)_2$ additive) = Content $Fe(OH)_2$ [%] x *0.6215*
- RIIC($Fe(OH)_3$) = *0.5226* → RIIC($Fe(OH)_3$ additive) = Content $Fe(OH)_3$ [%] x *0.5226*
- RIIC($Fe_2O_3 \cdot 3H_2O$) = *0.5226* → RIIC($Fe_2O_3 \cdot 3H_2O$ additive) = Content $Fe_2O_3 \cdot 3H_2O$ [%] x *0.5226*

Examples:

1. Additive X: 60% FeO → RIIC(Additive X) = 60% x *0.7773* = 46.6%
2. Additive Y: 40% $FeCl_3$ → RIIC(Additive Y) = 40% x *0.3443* = 13.8%
3. Additive Z: 10% FeO + 20% Fe_2O_3 + 45% FeO(OH)
   → RIIC(Additive Z) = 10% x *0.7773* + 20% x *0.6994* + 45% x *0.6285* = 50.0%

Remark: RIIC(SBGx) > 60% (Analysis March 2023)

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Comparison table of chemical equations with different iron based additives:

Desulphurisation agent	***RIIC [%]***	***Chemical equation***
Iron(II) oxide *SBGx*	77.73	$FeO + H_2S \rightarrow \mathbf{FeS\downarrow} + H_2O$
Iron(III) oxide *SBGx*	69.94	$Fe_2O_3 + 3H_2S \rightarrow \mathbf{2FeS\downarrow + S\downarrow} + 3H_2O$
Iron(II,III) oxide	72.36	$Fe_3O_4 + 4H_2S \rightarrow \mathbf{3FeS\downarrow + S\downarrow} + 4H_2O$
Iron(II) chloride	44.06	$FeCl_2 + H_2S \rightarrow \mathbf{FeS\downarrow} + 2\mathbf{HCl}$ [A]
Iron(III) chloride	34.43	$2FeCl_3 + 3H_2S \rightarrow \mathbf{2FeS\downarrow + S\downarrow} + 6\mathbf{HCl}$
Iron(III) oxide-hydroxide	62.85	$2FeO(OH) + 3H_2S \rightarrow \mathbf{2FeS\downarrow + S\downarrow} + 4H_2O$
Iron(II) hydroxide	62.15	$Fe(OH)_2 + H_2S \rightarrow \mathbf{FeS\downarrow} + 2H_2O$
Iron(III) hydroxide	52.26	$2Fe(OH)_3 + 3H_2S \rightarrow \mathbf{2FeS\downarrow + S\downarrow} + 6H_2O$
Iron(III) oxide trihydrate	52.26	$Fe_2O_3{\cdot}3H_2O + 3H_2S \rightarrow \mathbf{2FeS\downarrow + S\downarrow} + 6H_2O$
Also worth listing: Biological desulphurisation		
O_2 addition dosed correctly		$O_2 + 2H_2S \rightarrow \mathbf{2S\downarrow} + 2H_2O$
O_2 addition overdosed		$2O_2 + H_2S \rightarrow \mathbf{H_2SO_4}$ [B]
Side note: Grünsalz		
Iron(II) sulphate	36.76	$FeSO_4 + H_2S \rightarrow \mathbf{FeS\downarrow} + \mathbf{H_2SO_4}$

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

SBGx	*[%]*
FeO	> 35.0
Fe_2O_3	> 35.0
MnO	< 1.0
CaO	< 0.5
Al_2O_3	< 0.5
MgO	< 0.5
Cr_2O_3	< 0.2
Zn	< 0.1
Cu	< 0.1
NiO	< 0.1
K_2O	< 0.05
CoO	< 0.05

Analysis March 2023

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

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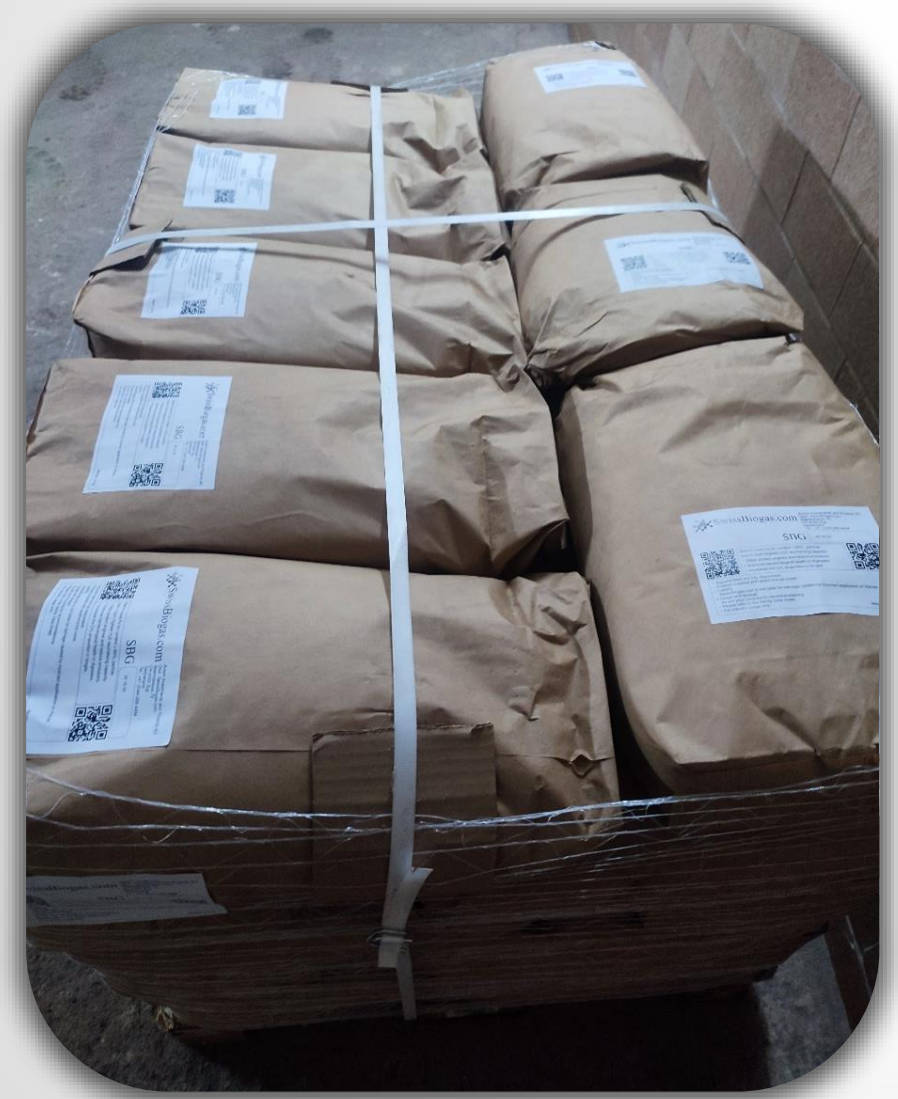

How we pack and ship:

Delivered in powder form in

- 20 kg bags or as per
- individual requirements

Please contact your agent for availability.