

Inorganic Specialty Chemicals

Chromate Reducers for the Mortar Industry



Topics

- The Chromate Issue and Legislation
- Reduction Technologies in Cements
- Long Term Cr(VI) reduction effect in Cement formulations
- Stannous Sulphate, its performance and stability
- Influence of Tin(II) based Cr(VI) Reducing Agents on Mortar properties
- Conclusion

The Issue....

Cr(VI) in Cement:

- Raw materials
- Secondary fuels
- Oxidative conditions in the cement kiln

**Total Chromium content in Cement:
50 – 200 ppm,**

Soluble Chromium: 0 – 40 ppm



The Issue.....

- continuous contamination of the skin with cement
- natural barrier function of the skin is overwhelmed
- the skins gets dry and cracked
development of an irritational eczema
- the barrier function of the skin is permanently disturbed
- Chromate Ions penetrate into deeper layers of the skin
- Sensibilisation by Chromate
- development of an allergic contact eczema



The consequence: European regulation

L 178/24

EN

Official Journal of the European Union

17.7.2003

**DIRECTIVE 2003/53/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 18 June 2003**

amending for the 26th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (nonylphenol, nonylphenol ethoxylate and cement)

(Text with EEA relevance)

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE
EUROPEAN UNION,

Having regard to the Treaty establishing the European Com-

- (4) In order to protect the environment the Commission is invited to consider an amendment to Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (7), with a view to estab-

European Legislation:

(6) Scientific studies have also shown that cement preparations containing chromium VI may cause allergic reactions in certain circumstances, if there is direct and prolonged contact with the human skin. All uses of cement bear the risk of direct and prolonged contact with the human skin, with the exception of controlled closed and totally automated processes.

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(9) In order to protect human health, it therefore appears necessary to restrict the placing on the market and the use of cement. In particular, the placing on the market and the use of cement or cement preparations containing more than 2 ppm chromium VI should be restricted in the case of activities where there is a possibility of contact with the skin. In controlled closed and totally automated processes this is not the case, and they should therefore be exempted. Reducing agents should be used at the earliest possible stage, i.e. at the point of cement production.

**The effect of Cr(VI) is proven,
Reducing agents should be used !**

Reduction Technologies

Agent	FeSO ₄	SnSO ₄	Sb ₂ O ₃	Na ₂ S _x
State of aggregation	Solid	Solid, liquid, dispersion	Dispersion	liquid
Market Share	#1	#2	Small	Very small
Cost /kg	Cheapest	Most expensive	Expensive	cheap
Consumption per to Cement	Highest	Low	Low	high
Key argument	Efficient & cheap	Most efficient, and long term stable, small CAPEX	Efficient, small CAPEX	Cheap, small CAPEX
Key problem	Long term stability, handling	Price	Only dispersion, Toxicity	Only liquid, Long term stability
Toxicity	No	No	Suspected cancerogenic	Corrosive, danger of H ₂ S development

Addition of Chromate Reducing Agents

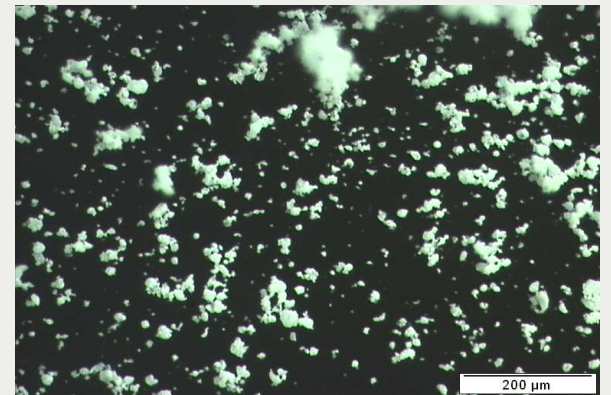
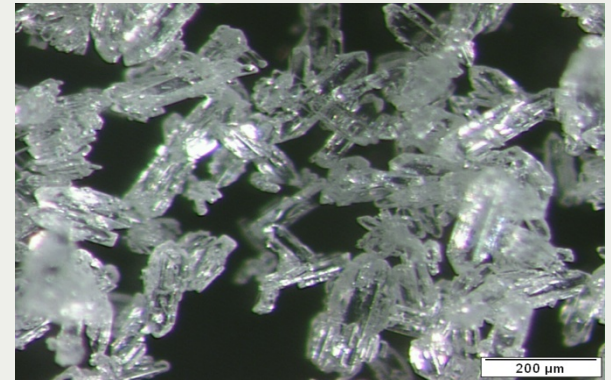
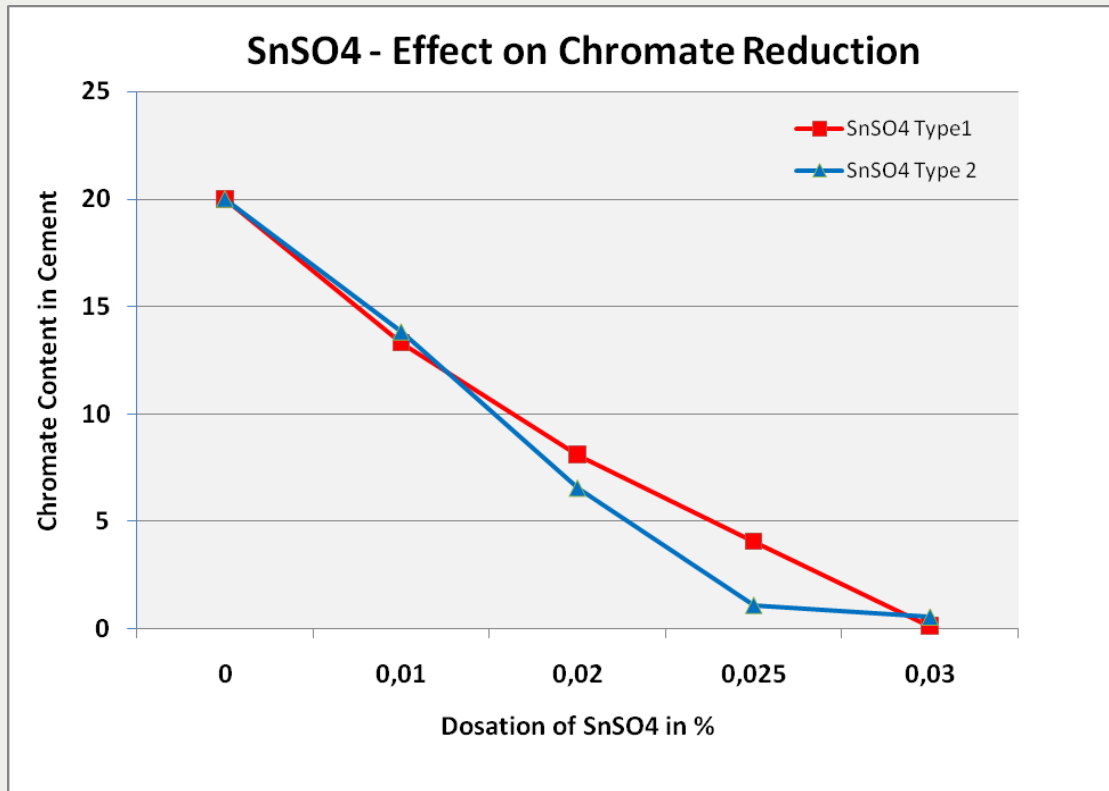
typically into the cement mill to ensure homogeneous distribution:



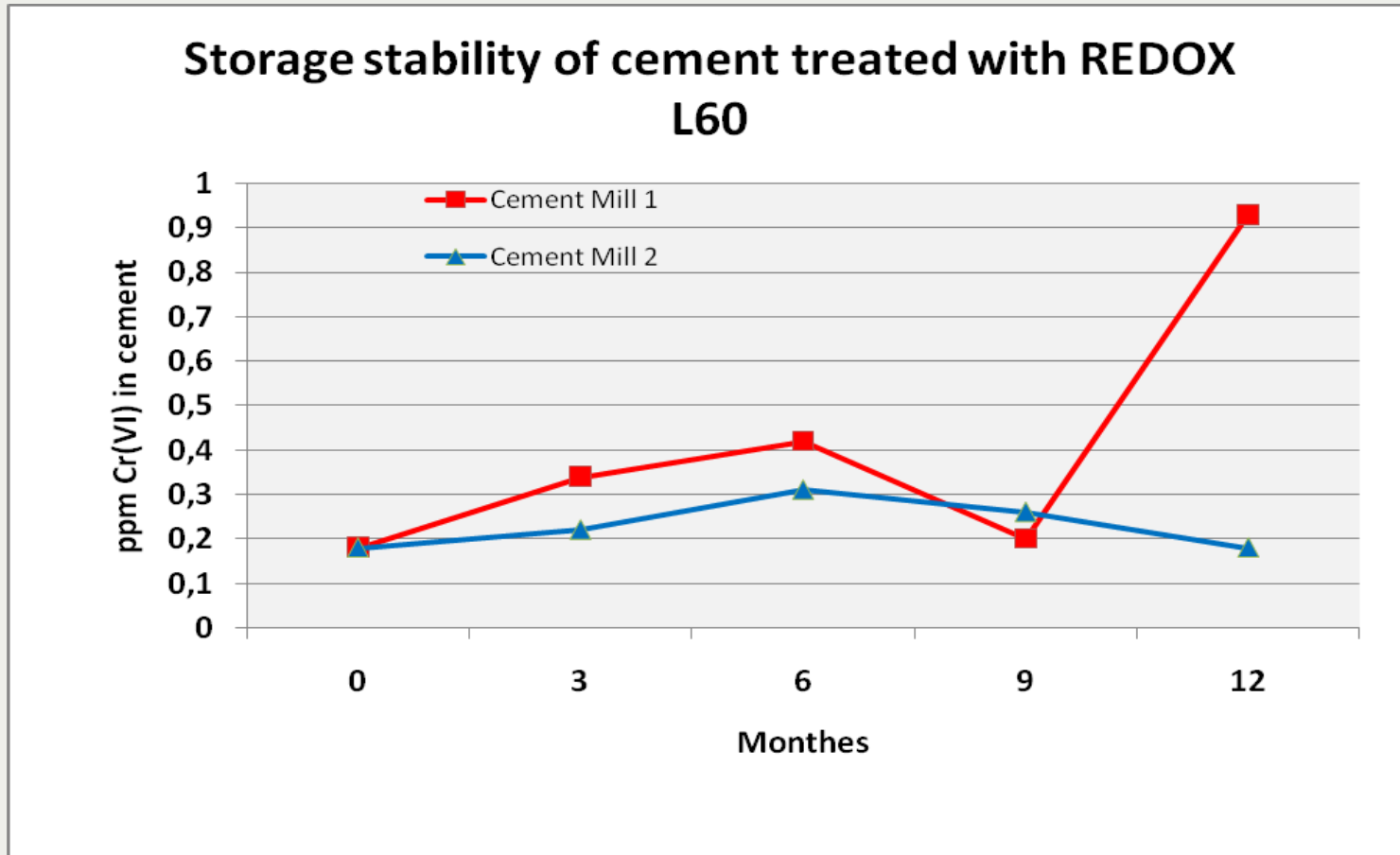
Feeding a liquid additive

Chromate Reduction Efficiency

- Cr(VI) reduction in dependency of SnSO₄ level



Chromate Reduction Efficiency



Consequences for the Dry Mix Industry

If Cement is already supplied with a chromate reducing agent incorporated,

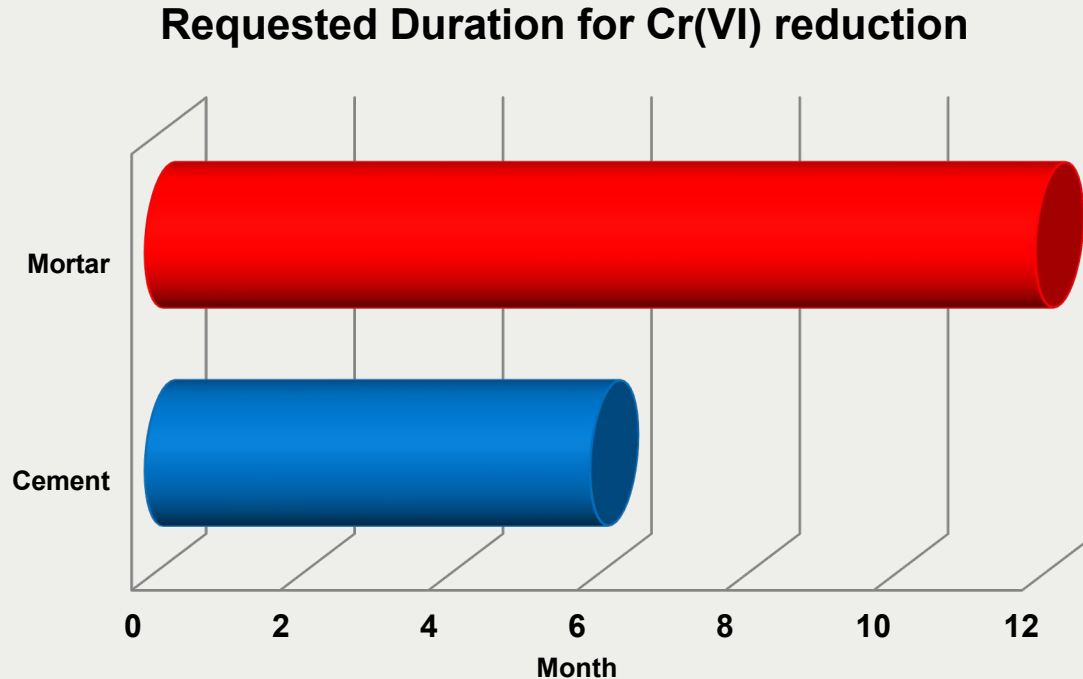
why should the Dry Mix Industry worry?

Long Term stability of the reduction effect in cement

Agent	FeSO4	SnSO4	Sb2O3	Na2Sx
Dosation per 1 ppm Cr(VI)	500 gr/to (*)	60 gr/to	65 gr/to	300 gr/to
Cr(VI) Reduction Efficiency	Low	Very high	High	medium
Long Term Stability	3 – 6 month	6 - > 12 month	12 month	3 month

(*) calculated as FeSO4*7H2O

Issues for the cement based formulations



Dry Mix products need long duration of Cr(VI) reduction effect

Cements are delivered mostly with a max. stability between 3 and 6 month

Solution: treatment of Dry Mix products

Properties	Reducing Agent for direct Feeding	Reducing Agent for Premix Process
Product	Formulated	Pure SnSO ₄
SnSO₄ content	10 %	95 – 100 %
Appearance	Grey free flowing powder	Crystalline
Stability	Excellent	Quality depending
Dosation for 10 ppm Cr(VI) in cement	1300 gr/to	130 gr/to
Dosation in Dry Mix products	0.1 – 0.2 %	0.01 – 0.02 %
Storage stability in Dry Mix products	> 12 month	12 month

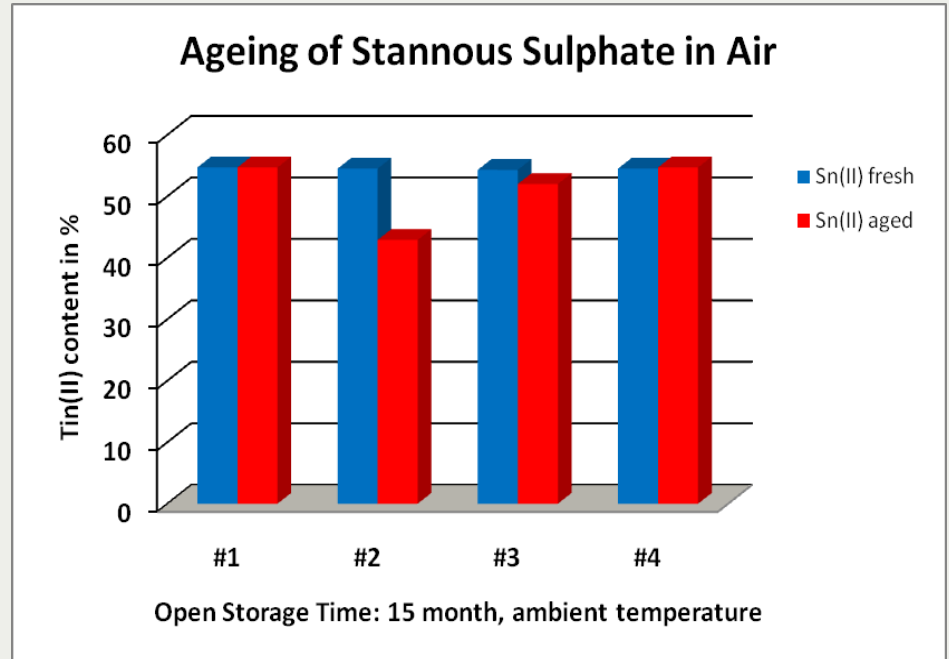
Influence on Chromate Reduction Efficiency

Efficiency of SnSO_4 based Reducing Agent is depending on:

- Type and Quality of SnSO_4
- Content of free Lime in cement and mortar
- Additives
- Raw materials

Chromate Reduction Efficiency

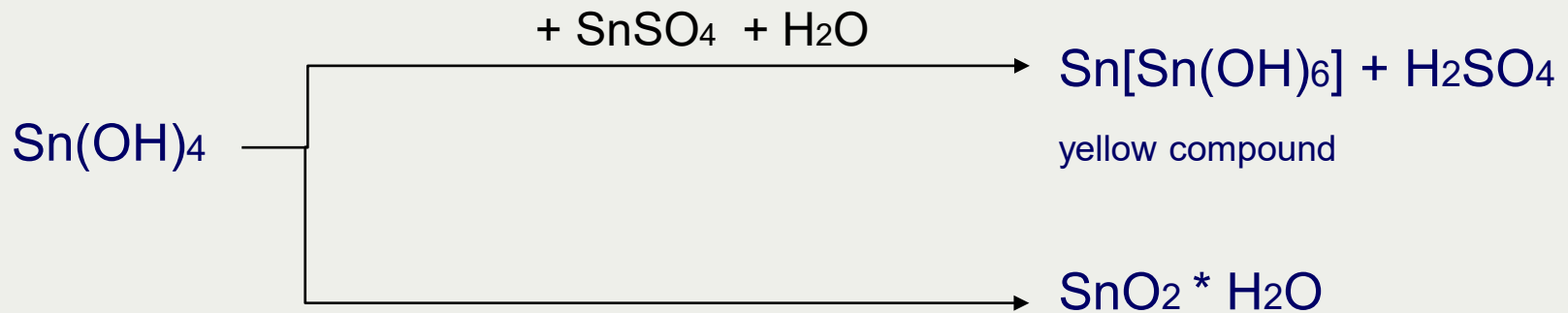
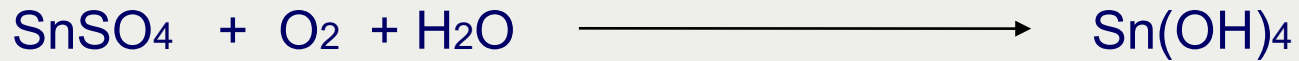
- Quality of Stannous Sulphate



**SnSO₄ is stable, but quality has to be monitored,
Yellow material is at the end of the shelf life**

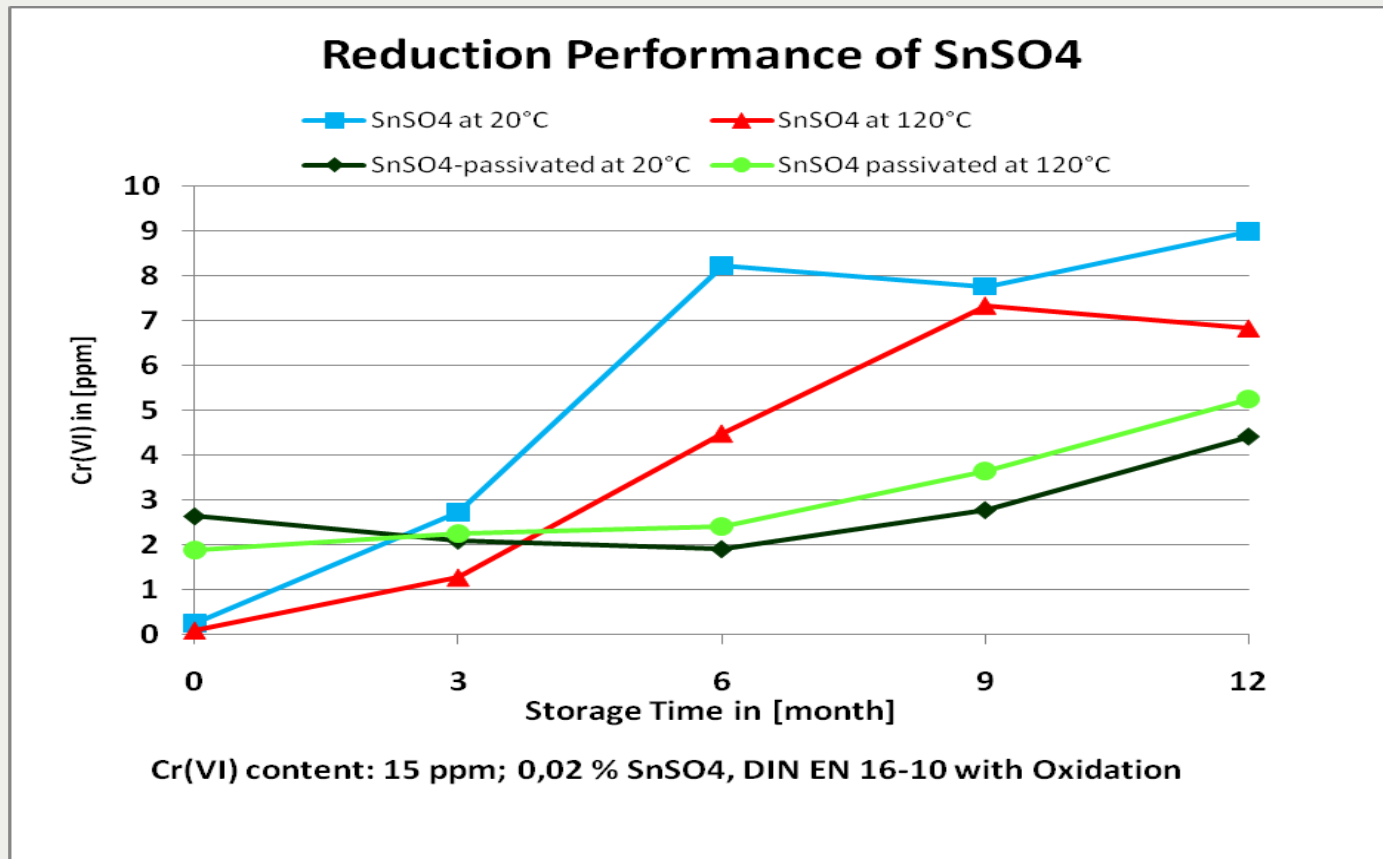
Ageing of Stannous Sulphate

- By Oxidation / moisture



Chromate Reduction Efficiency

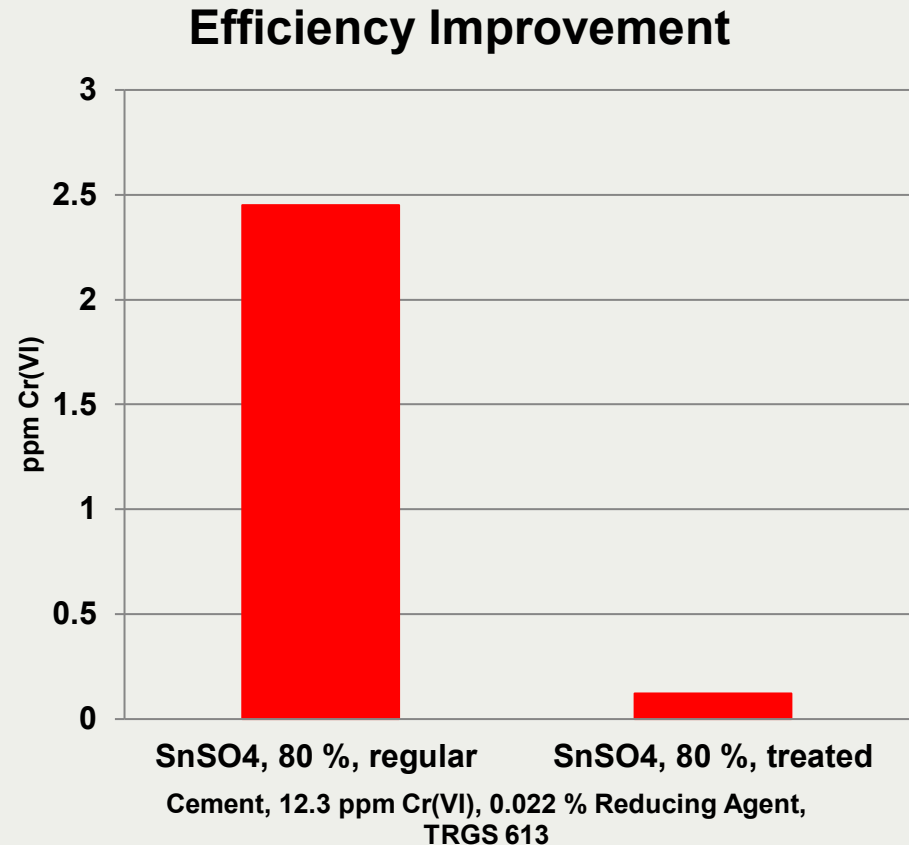
- Quality and Type of Stannous Sulphate



Chromate Reduction Efficiency

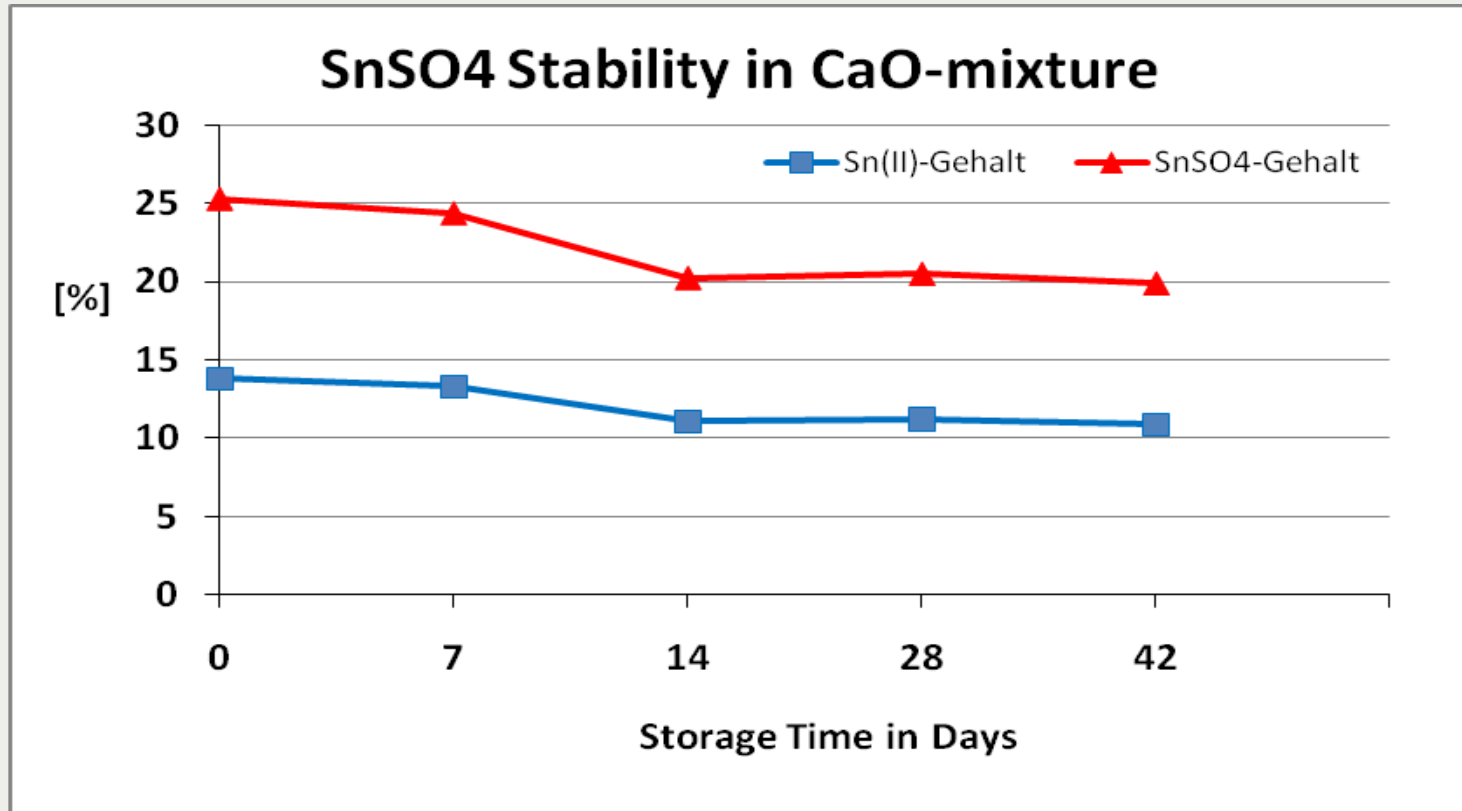
Quality of SnSO₄ is key feature
for the long term performance !

Treated SnSO₄ offers improved
Reduction efficiency by
cutting activity losses through
Oxidation and Alkalinity.

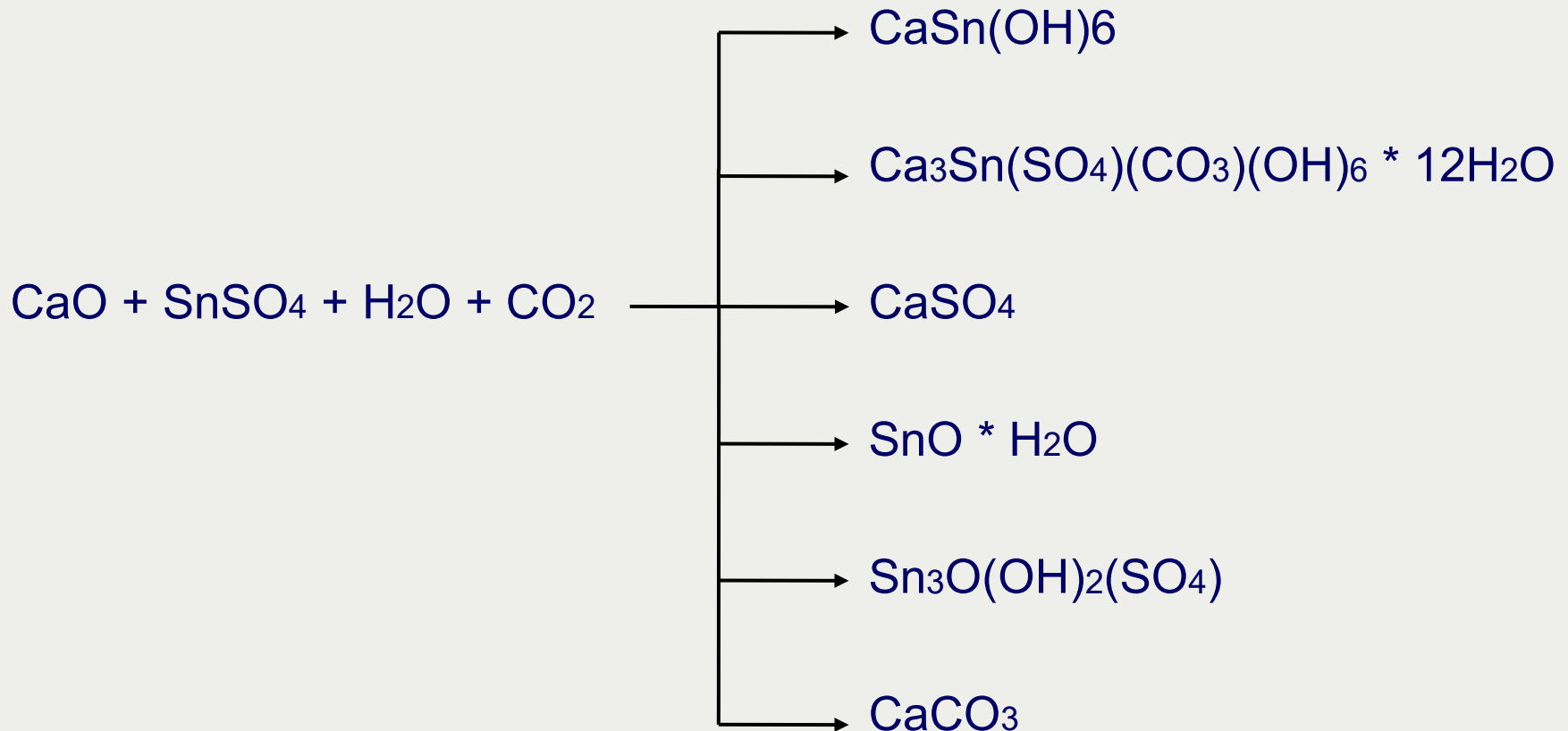


Chromate Reduction Efficiency

- Effect of free lime in cement/ mortars on Stannous Sulphate



CaO triggered decomposition of SnSO₄



Detected by X-Ray diffraction of 1:1 CaO – SnSO₄ mixtures

Conclusion

Long Term Reduction Ability of Stannous Sulphate is influenced by:

Ageing:

depending

- on quality of SnSO₄ and
- on oxidation / moisture

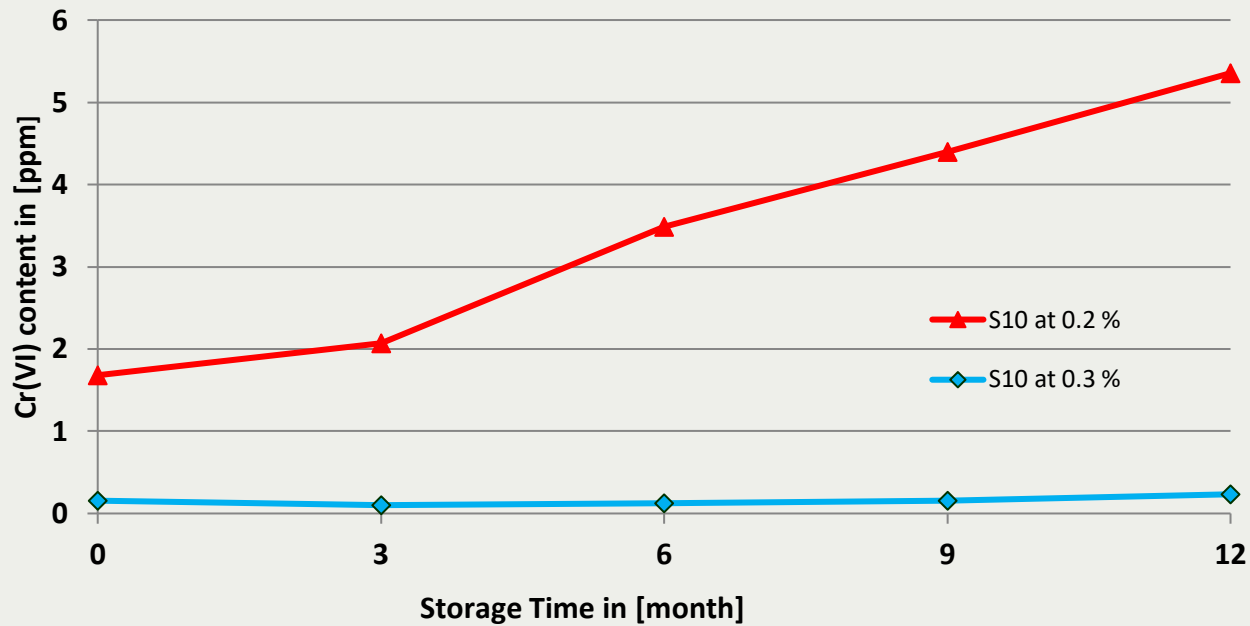
Decomposition:

depending

- on alkalinity, espec. on free Lime content
- on other ingredients

Solutions for improved performance

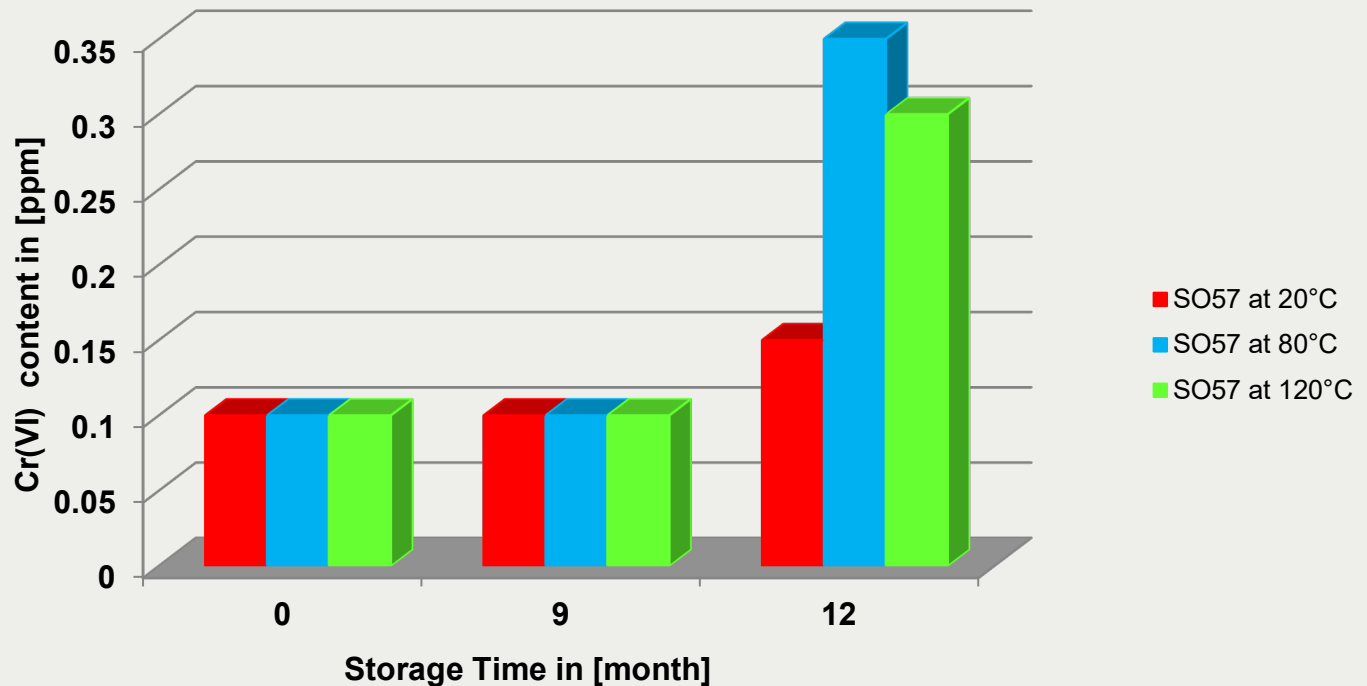
SnSO₄ with inorganic stabilizer



Cr(VI) content: 17,6 ppm; DIN EN 196-10

Solutions for improved performance

New Tin(II) based Chromate Reducing Agent



Cr(VI) = 17.8 ppm; 0,03 % Chromate Reducer, DIN EN 196-10

Influence of Chromate Reducing Agents on Mortar

- SnSO_4 reducing agent can influence mortar properties like

performance of methyl celluloses

and can lower

- water retention

- flow properties.

Reason: complex formation
between SnSO_4 and MC



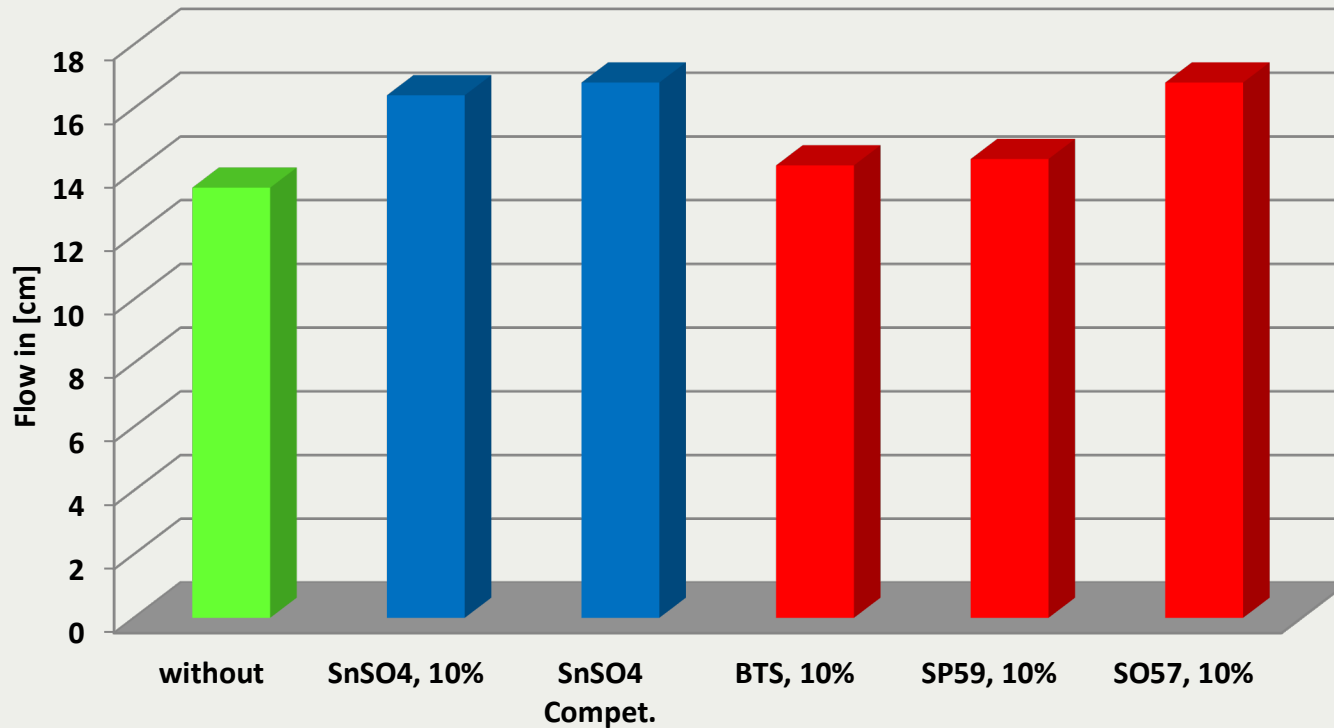
Result: Dependency on SnSO4 content?

SnSO4 content	SnSO4 content in mortar	Diameter vert.	Diameter horiz.
No additive	0 ppm	13.5	13.2
0 % (only stabilizer)	0 ppm	13.1	12.9
5.5 %	110 ppm	16.2	15.1
7.4 %	148 ppm	16.9	14.8
10 %	200 ppm	16.5	16.1
80 %	1600 ppm	15.8	14.5

- **System: IP 610 A, 10 hubs, 0.2 % Cr(VI)-Reducing Agent; 20.5 % water**

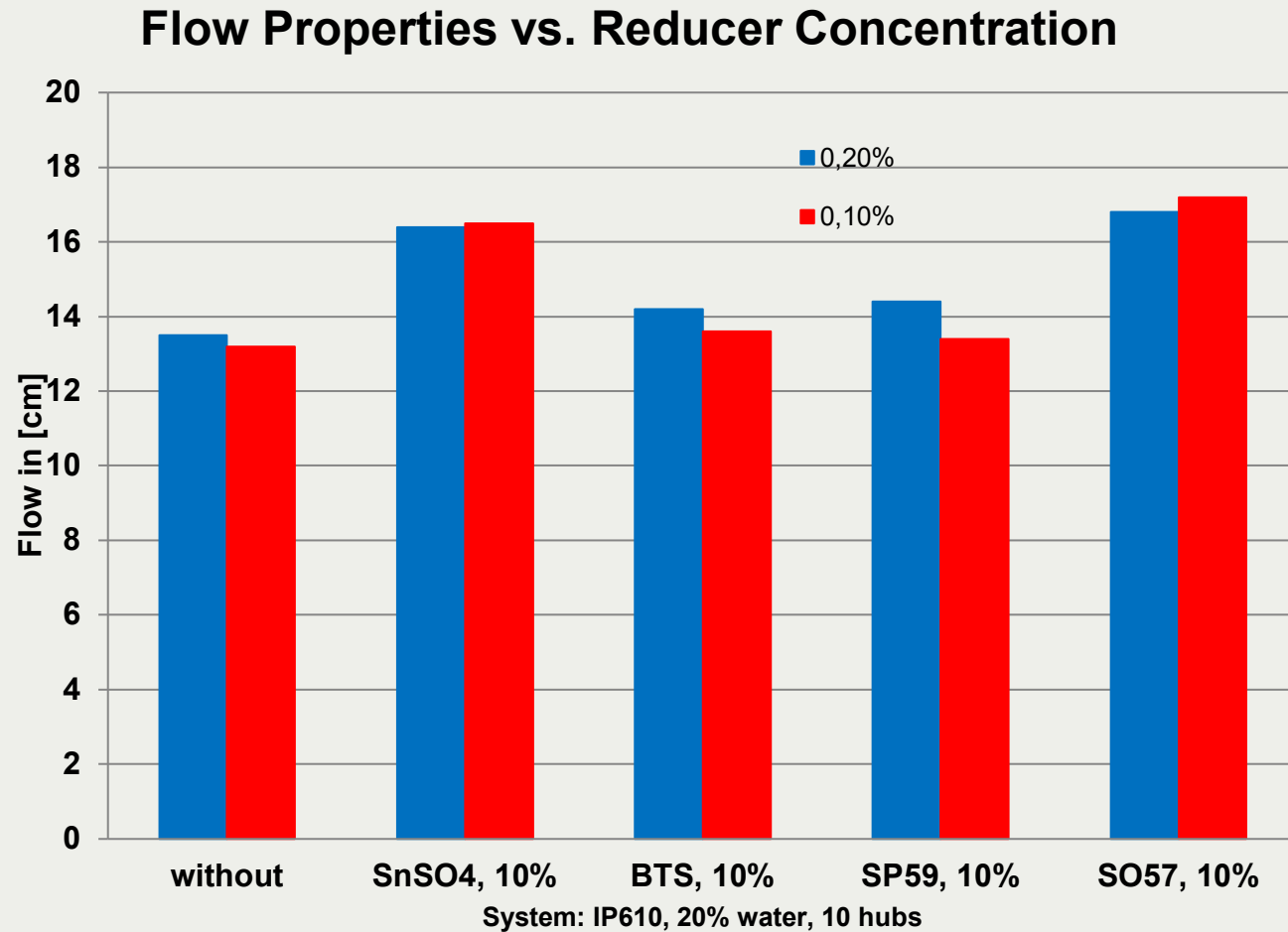
Influence of Cr(VI) Reducing Agents

Consistency Test: Flow Properties

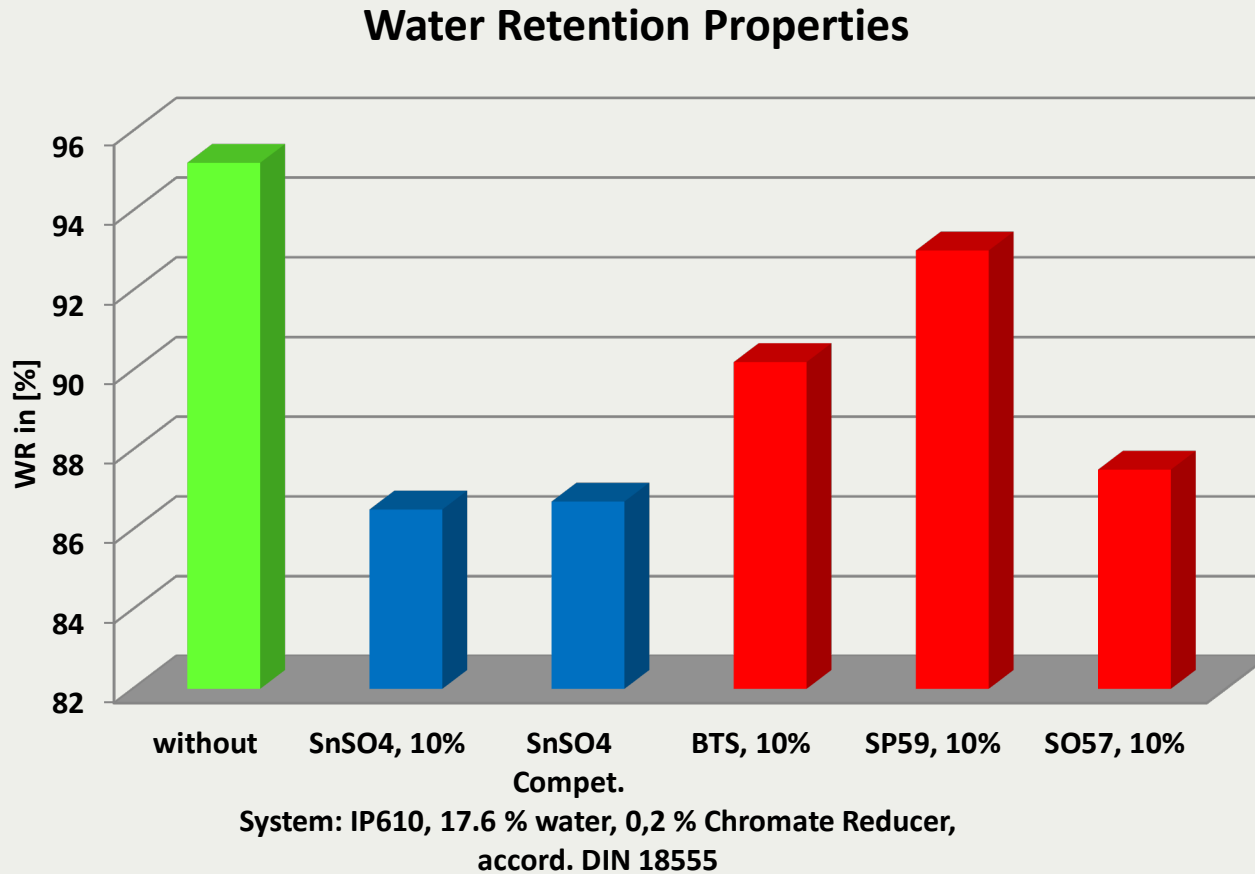


System: IP 610, 20 % water, 0.2 % Chromate Reducer, 10 hubs,

Influence of Cr(VI) Reducing Agents



Influence on Water Retention Properties



Conclusion

- Stannous Sulphate offers Cr(VI) reduction efficiency for more than 12 month.
- Activity losses of SnSO₄ can be reduced by improved manufacturing methods and addition of stabilizers.
- New Tin(II) based Chromate Reducing Agents have been developed which deliver improved performance
 - for - Cr(VI) efficiency
 - Flow properties
 - Water Retention in mortars.

Thank you very much for your attention:

For any questions:

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Chromate Reducing Efficiency

Product	Sn(II)-content [%]	5 ppm Cr(VI)-content	10 ppm Cr(VI)-content	20 ppm Cr(VI)-content
SnSO4 crystalline/powder	54.5	0.06 kg	0.13 kg	0.25 kg
SnSO4 solution	10.0	1,00 kg	not recommended	not recommended
REDOX BTS	70.0	0.046 kg	0.09 kg	0.18 kg
REDOX S10	5.4	0.6 kg	1.3 kg	2.6 kg
REDOX S80	43.6	0.08 kg	0.16 kg	0.32 kg
REDOX S95	53.0	0.065 kg	0.13 kg	0.26 kg
REDOX SO57	57.2	0.055 kg	0.11 kg	0.22 kg
REDOX SP59	59.0	0.055 kg	0.11 kg	0.22 kg
REDOX L60	32.0	0.15 kg	0.30 kg	0.60 kg
REDOX L32	18.0	0.3 kg	0.6 kg	not recommended

per 1 to of cement

TIB Chemicals: leading in tin chemistries

- Production of tin chemicals for more than 100 years
- Production of Stannous Sulphate for more than 30 years
- Two production sites:
 - Mannheim, Germany
 - San Luis Potosi, Mexico
- Dedicated to high quality and innovative manufacturing processes
- ISO certified

SnSO₄ powder / REDOX production plant in Mannheim



SnSO₄ powder unit in Mannheim



TIB Chem Corp. Mexicana



