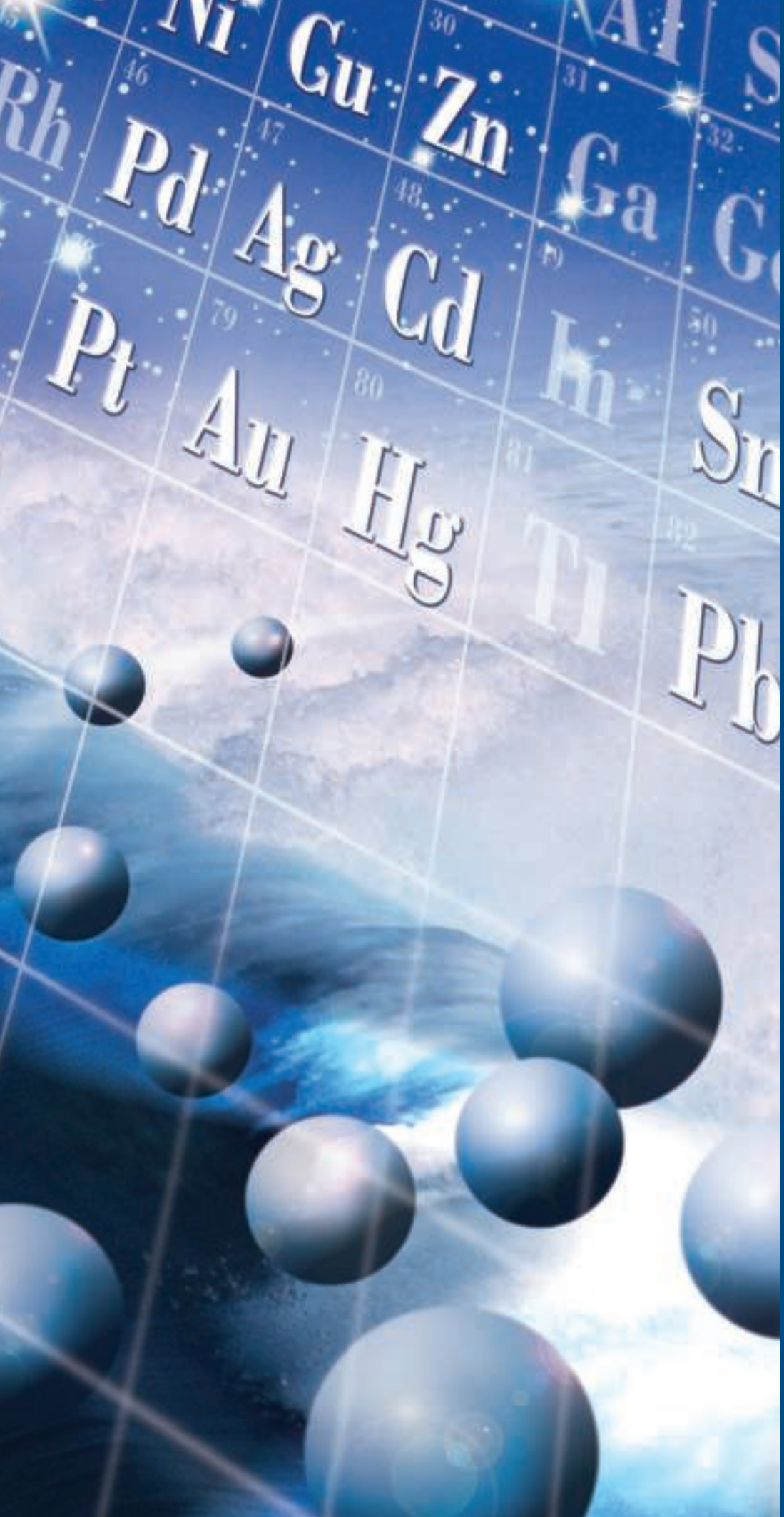


METALSORB™

Heavy Metal Chelating Agents

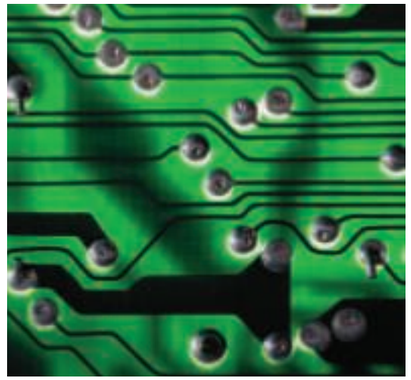
SNF FLOERGER®

METALSORB™ Sulfur based chelating agents

1 - Presentation

During the last few decades, legislators worldwide have instituted regulations to protect the environment from various contaminants, including heavy metals. Heavy metals are present in all kinds of effluents and flue gases. Their acute toxicity at very low doses and their trend to accumulate in the living organisms explain the growing need for heavy metals remediation in effluents as well as the increasingly strict regulations met worldwide. Industrial treatments able to reach the low levels required are chemical precipitation, ion exchange, adsorption, electrolysis and many sorts of filtration.

METALSORB™, is a range of sulfur based chemical precipitants allowing to reach these very low levels of heavy metal easily.



2 - Main Sources of Heavy-Metals

The number, the type and the levels of heavy metals found in water vary with the source of the effluents. We can distinct 2 main cases:

A -Process waters generally contain only one or two metals at high levels. The metal found in water is related to the process used. One could mention surface treatment baths with chromium, cadmium, nickel copper, zinc, tin, silver. Insecticide and herbicide production use copper, pigments and dyes will use zinc and cadmium as for the paint industry, tires production use cadmium, batteries can be made of lithium, zinc, nickel cadmium. When the metal content exceed a certain level or when the active ingredient is in insufficient quantity, water must be discarded and treated before recycling or being discharged. In those cases, the typical metal content can be up to grams per liter. The trend today is to separate the metal and recycle it, if possible, to improve economics.

B -Wastewaters generally contain all sorts of heavy-metals at low levels, typically milligrams per liter. The low levels and the numbers of metals eliminate the alternative of recycling. Wastewater can be rain water, wash water, scrubbing water,... Solvent and garbage **incinerators** are big producers of wastewater charged with all kind of metals as the flue gases are frequently scrubbed with water to remove volatile metals Extraction industry generates also big quantities of water rich in zinc, lead, arsenic, ...

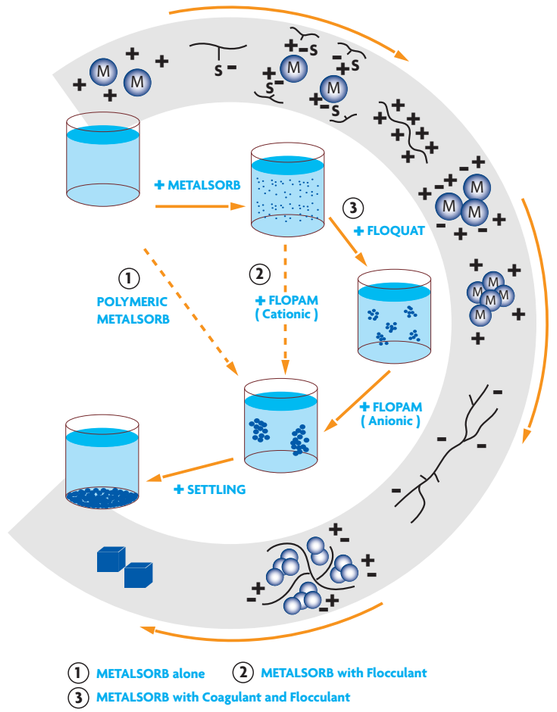
3 - Chemical Precipitation

This technique is still the longtime standard. Basically, a chelating agent (anionic) that readily bond with the metal in the dissociated form (cationic) is added to the water and forms an insoluble compound that precipitates. Polyelectrolytes are then added to increase flocs size until big enough to be removed from the treated stream through settling or filtering. The efficiency of this chemical precipitation is proportionnal to the residual solubility in water of the complex formed. Indeed, the previously called insoluble precipitate has a residual solubility dependant on the nature of the precipitant, as shown in the table below.

Metal	Carbonate	Hydroxide	Sulfide
Ag	5	16	4×10^{-15}
Hg	10^{-2}	6×10^{-13}	10^{-36}
Ni	2	4×10^{-3}	6×10^{-7}
Pb	6×10^{-6}	3×10^{-7}	8×10^{-13}
Zn	10^{-3}	5×10^{-4}	5×10^{-7}

Highest metal-removal power

ppm of residual metal in treated water after chelation with various precipitants



The occurrence of hydroxide and carbonate precipitation is justified by their low costs, they can be performed by a simple pH adjustment (eg. caustic or lime).
But,

- The precipitates are in the form of light tiny flocs requiring an extra coagulation/flocculation.
- Large volumes of sludge are generated, inducing additional waste-disposal costs.
- Regulation requirements are not always met using hydroxide and carbonate precipitation alone.
- Each dissolved metal has its own distinct pH level for maximum hydroxide precipitation. Because metal hydroxides are increasingly soluble above or below their individual maximum precipitation point, even a slight pH adjustment to precipitate one metal may put another back into solution.

4 - Precipitation with Dithiocarbamates

As seen in previous table , sulfide precipitation is the most efficient precipitation technique. The solubility is even low enough to destabilize soluble complexes in some cases. The simplest sulfur compounds are sodium sulfide salts (Na_2S, NaSH). It is however not recommend to use them as these two inorganic salts release toxic gas when pH is acidic and represent a risk in case of accidental release or over-dosage. The best alternative to these traditional sulfide treatments is the dithiocarbamate precipitation.

The chelating group is still based on the sulfur chemistry but is, this time, chemically bonded to an organic molecule. SNF reagents of this group are known as **METALSORB™**. Various grades are available corresponding to various organic substrates. Actually, the dithiocarbamate functionality relates only to the remediation power through the residual solubility of the metal complex. The organometallic precipitates relates more to the floc structure.
On one hand, the small organic molecules are highly active and are commercialized at high solid content but the precipitates formed request addition of polyelectrolytes to get a floc big enough for easy separation.
On the other hand, when you increase the size of the organic substrates, the active content must be reduced. The precipitate can however directly be separated from the water through settling or need only little addition of flocculant.

METALSORB™ provides an easy, flexible and cost-efficient solution to heavy-metaremediation.

METALSORB™ are water-based solution. The products are ready-to-use without prior dissolution or expensive make-up equipment. The dithiocarbamate group being chemically grafted on an organic structure, no free sulfurs and no toxic gases are released.

METALSORB™ is a very efficient precipitant of Heavy-Metals from waste streams producing water meeting official legislation criteria. Apart from Heavy-Metals remediation, **METALSORB™** has other usefull properties:

The wide range of molecular architecture available allows the formation of flocs adapted to any plant design. Carry-over of flocs in overflows that would put Heavy-Metals back into the treated water are reduced and suppressed by addition of flocculants and/or coagulants. The large floc size that can be reached ensures rapid settling and easy dewatering of the sludge. Coagulant and/or flocculant consumptions can be reduced and sometimes suppressed. Using the appropriate **METALSORB™** grade. The formation of dense, compact sludge, minimize disposal costs.

METALSORB™ is applicable under a wide range of pH (generally between 3 to 10 and preferably 4 to 9) and temperature.

METALSORB™ is effective against a wide array of metals and removes various co-existing Heavy-Metals at the same time. The chelating power of the dithiocarbamate group allows the direct precipitation of complexed or chelated metals. Chemically stable sludge are generated avoiding any secondary pollutions.

In particular, **METALSORB™** has proven to be very effective in the treatment of effluents arising from:

- Garbage incineration facilities
- Solvent incinerator
- Printing factories
- Leather products factories
- Iron and steel manufacturers
- Metal processing industry
- Electronics industry
- Photographic industry
- Automotive industry
- Chemical industry
- Power stations
- Electroplating industry
- Refineries of non-ferrous metals ...

5 - METALSORB™ characteristics

Heavy Metals reacting with **METALSORB™**

IVb	Vb	VIb	VIIb	VII	Ib	IIb	IIIa	IVa	Va	VIa
Ti	V	Cr	Mn	Fe	Cu	Zn	Ga	Sn	As	Se
		Mo		Co	Ag	Cd	In	Pb	Sb	Te
		W		Ni	Au	Hg	Tl		Bi	
		U		Pd						

6 - Application Procedure

For a stream without soluble complexes, **METALSORB™** is added directly to the wastewater at a **water pH between 3 to 10**. The dithiocarbamate functionality reacts with the dissociated Heavy-Metal ion to form an insoluble complex and a floc will form.

The dosage of chelating agent can be determined based on the composition of the water to be treated, the treatment already in place or a jar test.

When the pollution level is unknown, SNF's technical assistance team can provide special services including in-depth analysis of a water sample at SNF's headquarters.

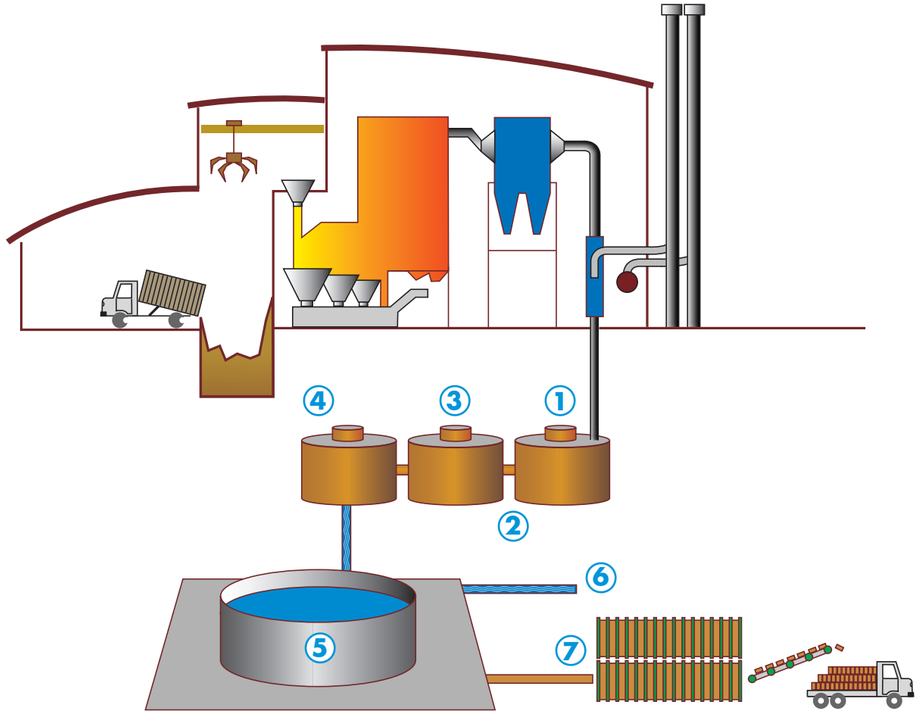
If necessary, a coagulant (**FLOQUAT™**FLB, polyamines or polyDADMAC, an aluminum or a ferric salt) can be added to increase the size of the floc. To further enhance floc size and settling speed an anionic flocculant is sometimes added. A cationic polymer can also be used in specific cases.

When the Heavy-Metals are in the form of complexed Heavy-Metals in the wastewater (citrates, phosphates, thiosulfates, EDTA, cyanates...), contact SNF Technical Assistance for local support.

METALSORB™ can effectively be removed from effluent discharges by filtering through activated carbon (sold by SNF Floerger). This treatment is especially useful when excess **METALSORB™** have been used to reduce soluble metals to very low levels.

Schematic for waste water treatment at a garbage incineration plant: Effluent containing soluble metal, using METALSORB™

Because all plants are different, this diagram is given for illustration only.
Please contact SNF technical assistance team for a customized service.



1. *Lime or caustic pretreatment : neutralisation and hydroxide precipitation of the wastewater coming from the scrubber*
2. ***METALSORB™*** *treatment : chelation of heavy metals dissolved in the wastewater*
3. ***FLOQUAT™*** *Coagulant (facultative) : growth of floc size*
4. ***FLOPAM™*** *Flocculant (cationic or anionic, facultative)*
5. *Settling tank*
6. *Sewer discharge : Most soluble metal concentration below regulation threshold*
7. *Filter : sludge disposal or metals reclamation processing*