



Mining Solutions Antiprex[®] E

The efficient descaling solution
for the mining industry

 **BASF**
We create chemistry

BASF's Mining Solutions at a Glance

BASF's Mining Solutions business offers a diverse range of mineral processing chemicals and technologies to improve process efficiencies and aid the economic extraction of valuable resources.

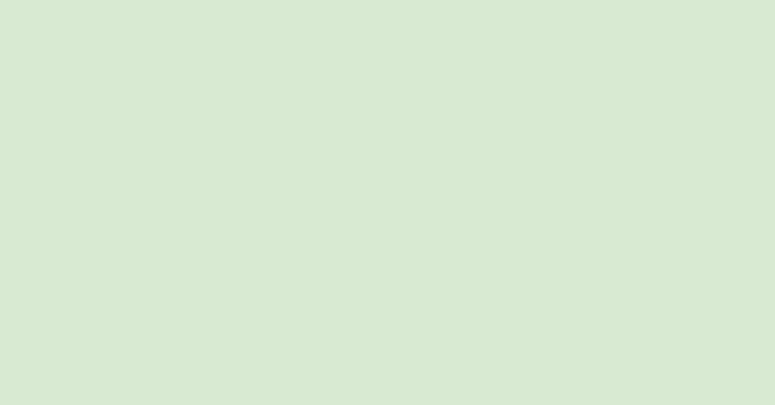
We offer our products and technology solutions to the global mineral processing industry along with expert advice and technical support. Our global team is driven by a common goal to provide the best sustainable solution to meet our customer's processing needs. With technical representation in over 100 countries, BASF provides support on a global, regional and local basis.

Our offer includes reagents, equipment, process technologies and expertise, focusing on applications such as solid liquid separation, solvent extraction, tailings management, flotation, grinding and materials handling.

Antiprex® E

Scale is a common problem in mining operations. Scale formation in pipelines, tanks, heat exchangers, pumps and sprayers results in reduced flows, increased energy costs, decreased heating or cooling efficiency and costly downtime for cleaning and scale removal. While scale formation can often be greatly reduced (depending on the system chemistry) by the appropriate use of BASF Antiprex® and Sokalan® antiscalants, sooner or later there is nearly always a need to remove existing scale.

Some scale minerals are amenable to acid cleaning and traditional strong mineral acids and weak organic acids have been used for this purpose for many years. Antiprex® E is a product well suited to this application as it is a strong acid, dissociating completely for faster results than other organic acids, whilst being less corrosive and safer to handle than traditional mineral acids. Antiprex® E is now available to the mining industry. The primary area of application is the safe, efficient removal of scale from pipelines with minimal corrosion of the pipeline itself. There may also be additional areas of application such as descaling pumps, heat exchangers, tanks and mixers subject to appropriate safety procedures.



Benefits of Antiprex[®] E

Antiprex[®] E is a high purity grade of methanesulfonic acid (MSA), manufactured by BASF's air oxidation process. This proprietary technology offers a number of significant benefits over MSA produced by the conventional chloroxidation route.

BASF's air oxidation process produces a high purity product which does not contain chloride ions. The presence of chloride in MSA products significantly increases corrosivity. Antiprex[®] E also offers significant advantages over traditional organic acids and mineral acids as outlined below.

Chemical benefits

Strong Acid: Antiprex[®] E is a strong acid with similar dissociation constant to sulfuric acid, so offers increased reaction rates and more rapid descaling action than typical organic acids while being much less corrosive to metals and safer to handle than other strong acids.

Increased solubility of calcium: Many metals are more soluble as the methanesulfonate¹ than as the phosphate or sulfate. This offers more flexibility in tailoring solution strength to suit the application. Stronger solutions can be used to increase reaction rates without precipitating out salts such as gypsum and apatite. Antiprex[®] E can solubilise more scale into solution.

Oxidation resistant: Antiprex[®] E can be used in strongly oxidising environments and in the presence of oxidising agents without decomposition.

Chemically stable: Antiprex[®] E is a non-oxidising acid which makes it safer for handling and suitable for the formulation of acid cleaning products for specialist applications. It can be formulated with other acids, corrosion inhibitors, oxidising and reducing agents, chelating agents and surfactants to provide optimal performance in descaling sensitive alloys.



¹ Methane sulfonate salts are also known as mesylate salts.

Benefits of Antiprex® E

Safety and handling benefits

Low corrosivity: Antiprex® E is significantly less corrosive than some other strong acids.

No gas phase corrosion: Unlike many other more volatile acids, such as hydrochloric acid, nitric acid or formic acid, the low vapour pressure of Antiprex® E means that it does not produce gas phase corrosion under normal conditions.

Ultra low VOC content: Antiprex® E has a very low vapour pressure and unlike carboxylic acids such as acetic acid and glycolic acid it is virtually free of volatile organic carbon content.

Odour free: The low vapour pressure of Antiprex® E means that unlike some other organic acids it is odour free.

No toxic vapours: Due to its low vapour pressure Antiprex® E does not produce toxic vapours and is safer and simpler to handle than acids such as hydrochloric acid and nitric acid.

Non-flammable: Unlike other organic acids, such as acetic acid, Antiprex® E is non-flammable.

Environmental benefits

Biodegradability: Antiprex® E is readily biodegradable according to OECD Guidelines 301 and 306, forming carbon dioxide, sulfate, water and biomass as degradation products.

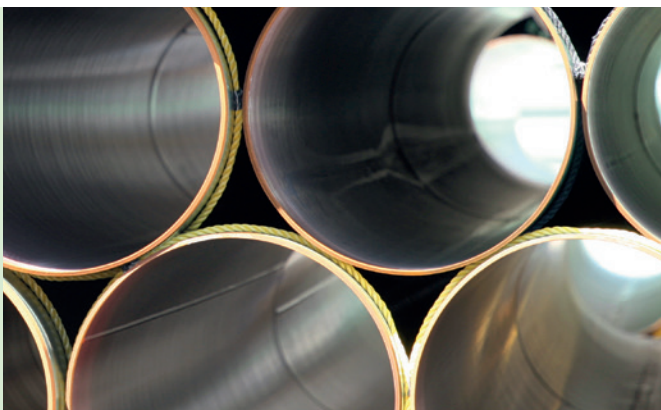
Very Low Chemical Oxygen Demand: Antiprex® E (Methane sulfonic acid) has the lowest oxygen demand for degradation of any sulfonic acid. Due to its resistance to oxidation, it also has a lower COD than readily oxidised organic acids such as acetic acid.

Does not contribute to eutrophication and algal growth: As Antiprex® E contains no phosphorus or nitrogen it does not contribute phosphates and nitrates to aquatic ecosystems.

Part of the natural sulfur cycle: Methane sulfonic acid is formed in nature by photochemical oxidation of dimethylsulfide in the atmosphere before returning in rain fall, where it is metabolised by bacteria in soil and sediments. The chemical is thus part of the natural sulfur cycle.

Halogen Free: Unlike hydrochloric acid and brands of MSA produced by the chloroxidation route, Antiprex® E is halogen free, has reduced corrosivity and does not contribute chloride ions to waste.

Low toxicological risk potential: while Antiprex® E is a strong acid, the lack of halogens, nitrogen and phosphorus give it a lower ecotoxicity potential than many other acids.



Target Processes and Ores

Calcite scale is most rapidly removed at ambient temperatures. Antiprex® E can also be used for the removal of gypsum, calcium phosphate and calcium oxalate scales but works best at elevated temperatures which may not be practical in long pipelines.

General descaling: The product can also be used for general descaling of other equipment.

Derusting: Antiprex® E can be used for derusting equipment however it works best at elevated temperatures and in rust removal formulations where corrosion inhibitors and synergistic blends with other acids are used. Additional information is available on request.

Ore types: As the target species is the scale, rather than the ore itself, Antiprex® E can be used with almost any ore type where scale formation is a problem, however specific types of process and ores need to be approached with caution.

Removal of Calcite from a pipe with 5% Antiprex® E solution.

- 1: Severe concentric scale has nearly closed the pipe.
- 2: Dissolution of the scale commences upon treatment with Antiprex® E.
- 3: Antiprex® E has excellent penetrative properties, liberating scale from the pipe wall, accelerating dissolution.
- 4: After 3 hours static soak time.

PIPELINE DESCALING



Processes Requiring Caution

Gold

Cyanide leaching of gold can result in calcite scale formation as pH control is often accomplished with lime and the leach solution pH is very high after cyanide addition. The use of Antiprex® E to remove scale in these circuits introduces the potential for contact of the strong acid with cyanide solutions, cyanide containing residues and potentially contamination of heap leach piles with strong acid. Great care would need to be taken to mitigate the risk of hydrogen cyanide gas evolution, which would pose a grave safety hazard to site personnel.

As Antiprex® E is highly oxidation resistant it can be utilised with hydrogen peroxide which is often utilised for cyanide destruction in tails. The application area of concern could also be flushed with a hydrogen peroxide solution prior to Antiprex® E exposure, to destroy any cyanide present. These measures may mitigate some of the risk although it is unlikely to eliminate it completely as the peroxide dose would be estimated based on the expected amount of cyanide present.

In the event of leakage, spills and other unexpected events or underestimation of the quantity of cyanide present, hydrogen cyanide gas generation could still occur. BASF do not recommend Antiprex® E in this application unless stringent risk assessment has been carried out covering all aspects of the application. This concern is common to all acid cleaning products in this context and is not unique to Antiprex® E.

Base metal concentrates

Metal sulfide concentrates may liberate hydrogen sulfide gas if treated with a strong acid such as Antiprex® E. It is likely that scale formed in concentrate pipelines will contain some concentrate inclusions, so some hydrogen sulfide evolution should be taken into account during the risk assessment process. Hydrogen sulfide gas is extremely toxic, heavier than air and its strong and distinctive odour disappears at lethal concentrations, as the olfactory receptors are saturated. As receiving vessels fill, hydrogen sulfide gas may overflow and settle in low lying areas such as access tunnels under tanks and sumps. Metals such as lead and zinc are also very soluble as their methanesulfonate salts so the spent cleaning solution would be expected to contain some level of heavy metals in solution, and may require further treatment prior to discharge.

Solvent extraction

Introduction of any new reagent in front of SX processes should include assessment of any potential for negative impacts downstream. As Antiprex® E does have some solubility in alkanes such as heptane, it is likely to be able to pass into the organic phase.

Target Scale Types

Dissolution times for less soluble salts such as calcium sulfate can be reduced by heating, increasing the concentration of Antiprex® E or in some cases by formulating with chelating

agents and other acids. The optimum blends depend upon the pipeline materials. Additional information is available on request.

	SCALE TYPE	COMMENTS
ACID – BASE (NEUTRALISATION) REACTIONS	Calcium carbonate	Calcium carbonate scales are very common and the dissolution rate with Antiprex® E make it suitable for use at ambient temperatures
	Iron hydroxide	Iron hydroxide deposits dissolve readily in Antiprex® E at room temperature
	Iron oxide – Rust	Rust removal is slower than hydroxide deposit removal, but rust removal is disproportionately faster as treatment temperature increases
	Extended contact time or heating beneficial	
DISSOLUTION REACTIONS	Calcium sulfate	Calcium sulfate scale can be removed with Antiprex® E however the dissolution rates are modest at room temperature and elevated temperatures will increase the dissolution rate substantially
	Calcium oxalate	Calcium oxalate scale can be removed with Antiprex® E, however dissolution rates are modest at room temperature and elevated temperatures reduce the dissolution time substantially
	Calcium phosphate	Calcium phosphate and iron phosphate scale can be removed with Antiprex® E however the dissolution rates are modest at room temperature and elevated temperatures will increase the dissolution rate substantially

Solution Strength Required

Typical solution strength

Antiprex® E is usually utilised as a 5–10% solution as the active acid. Antiprex® E is a 70% active solution as supplied. A dilution factor of seven gives a 10% active solution. A dilution factor of 14 gives a 5% active solution. Concentration can be varied to provide an adequate amount of reagent and a suitable volume of solution to ensure adequate contact time. Lower solution strengths will require extended contact time as dissolution rates decrease with decreasing acid concentration.

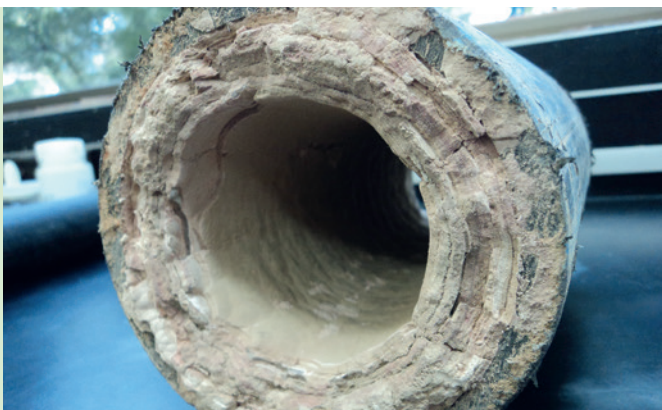
Use of the concentrated acid may result in the solution becoming saturated with calcium methanesulfonate resulting in reduced cleaning performance. Reaction rates are likely to be very rapid which may result in rapid generation of carbon dioxide and excessive pressure in the line.

Contact time

Adequate contact time between the acid and the scale is required in any descaling application. As with any chemical reaction, factors such as mixing, temperature, solution concentration and the surface area of the solid will all influence the reaction rate. An additional factor which may be overlooked is that in mining applications, scale is often impure. Impurities in scale can take two forms:

- inclusions, where scale growth is rapid particulate matter such as ore, concentrate, clays or iron hydroxide precipitates will be trapped in the growing scale and these inclusions can reduce the surface area available for the acid to attack, reducing the reaction rate.
- co-precipitation, occurs when sparingly soluble compounds are deposited together. The second salt may be less soluble in the acid, again slowing the rate of reaction. Calcium silicate is not uncommon in calcite scales and tends to make the scale surface harder and more acid resistant.

Depending on the scale composition and site specific conditions the required contact time may vary from a few minutes to a few hours. Laboratory testing can assist in establishing the likely dissolution rate for a particular deposit.



Calcite scale with particulate inclusions in a tailing disposal line.

Recycling of the Spent Solution

For neutralisation reactions, the spent cleaning solution may be re-used to clean a further section of line by the addition of more Antiprex® E. The practical limitation to re-using the solution is simply that it will eventually become saturated with calcium methanesulfonate, or other sulfonate salts. As the concentration of calcium methanesulfonate builds up the dissolution rate will also slow and the required contact time will increase. After three uses, a solution kept at 10% active free acid will have about half the saturation concentration of calcium methanesulfonate. Dissolution rates at this point would be expected to be significantly reduced.

For dissolution of sulfate and phosphate scales, recycling of the spent solution is not recommended due to the impact of ionic strength and common ions on the solubility product.

A large gypsum crystal formation resulting from a slow precipitation in a Ni/Co SX plant.



Safety Considerations

While many mineral processing operations have equipment and processes in common, there will always be a variety of differences in chemistry, engineering, process design and so on that make each site unique.

While Antiprex® E has many chemical, environmental and material handling benefits compared to other acids, it is still a strong acid. BASF recommends that a management of change procedure and full hazard identification and risk assessment process should be used to ensure that there are no unforeseen reactions or engineering issues.

Two examples of processes requiring caution; Cyanide leaching of gold and base metal concentrates as discussed on page 7.

- Where calcite scale is removed, carbon dioxide is formed as a product of the reaction. In most cases this will result in a pressure increase in the pipeline. Where pressure is contained, the carbon dioxide will tend to remain in solution until the pressure is released. Care should be taken to assess the pressure limitations of the equipment being cleaned.
- If the pipeline discharges into an open tank then foaming may be an issue and being heavier than air, the carbon dioxide evolved may overflow the tank in still conditions and settle to low points displacing air. Locations with limited ventilation such as access corridors beneath tanks may develop oxygen deficient atmospheres. This is a safety issue for any acid cleaning product, and is not specific to Antiprex® E.



- Antiprex® E has a coefficient of cubical expansion significantly greater than water. Care should be taken to avoid overpressurisation or leakage of equipment if sealed to allow for the thermal expansion in hot conditions.
- Antiprex® E is hygroscopic. Containers should be kept tightly sealed. If stored in open tanks the concentration of the acid will be reduced as moisture is absorbed from the atmosphere. Typically Antiprex® E under conditions of atmospheric pressure at 55% relative humidity and 23 °C would equilibrate at 49% active content compared with 70% in the sealed container. Increases in volume due to moisture absorption may result in overflow from tanks.
- Antiprex® E has a specific gravity of 1.35. This will result in increased loading on tanks and footings and increased head pressure in pipelines compared to water.
- BASF recommends that Antiprex® E be stored in accordance with the material safety data sheet and with AS3780-2008 or the local equivalent.

Calcium sulfate scale collected from a pregnant liquor pump.



Material Compatibility

Antiprex® E from BASF is less corrosive than other commercially available grades of methanesulfonic acid, due to the absence of halogen impurities.

Nonetheless, as with all strong acids, attention must be paid to the choice of materials for use with the acid. Corrosiveness depends to a large extent on parameters such as temperature and concentration. In general it is reduced by the presence of substances such as surfactants, oils and amines, but may be increased by halogens such as chlorides.

Suitable materials for use in conjunction with pure 70% methanesulfonic acid (Antiprex® E) are for example:

- Polyethylene, polypropylene
- Selected Palatal® grades (polyester, polystyrene resins)
- Teflon® (PTFE)
- Glylon® (modified PTFE)
- Glass, enamel, ceramics
- Tantalum, zirconium
- High Quality Special Steels such as
 - 1.4539 [904L; X1NiCrMoCu25-20-5]
 - 1.4571 [316Ti; X6CrNiMoTi17-12-2]
 - 1.4591 [Alloy 33; X1CrNiMoCuN33-32-1]



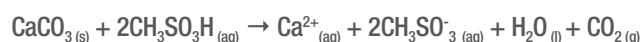
Compared with other strong acids, methanesulfonic acid is less corrosive: if similar quantities are used, the corrosion rates of methanesulfonic acid are normally a fraction of those of sulfuric acid or hydrochloric acid.

Because of the low vapour pressure, under normal conditions, there is no gas phase corrosion with Antiprex® E – in contrast to acids such as hydrochloric, nitric and formic acids.

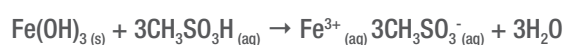
The corrosion impact of strong acids can be significantly reduced by the use of suitable corrosion inhibitors. More information on corrosion inhibitors is available on request.

Equations and Calculations

Equation 1: Reaction of calcium carbonate with Antiprex® E



Equation 2: Reaction of iron(III) hydroxide with Antiprex® E



Equation 3: Reaction of iron(III) oxide with Antiprex® E



Equation 4: Mass of scale in pipe

$$\text{Mass of calcite in pipe (kg)} = \pi \times (R_1^2 - R_2^2) \times L \times d \times \% \text{ calcite}$$

Where R_1 = the radius of the pipe (m)

R_2 = the radius of the pipe – the thickness of the scale deposit (m)

L = the length of the pipe (m)

d = density of the scale (kg/m^3)

% calcite = the proportion of the deposit by mass which is calcite.

Equation 5:

Volume of solution required for a given contact time

$$\text{Required volume of acid solution} = \frac{\text{Volumetric flow rate desired contact time} \times \text{m}^3 \times \text{hr}}{\text{hr}}$$

Table 1: Antiprex® E requirements for different scale types

NAME	FORMULA	FORMULA MASS/G.MOLE ⁻¹	MOLE RATIO 1:X	ANTIPREX® E REQUIRED PER UNIT MASS OF SCALE
Calcite	CaCO ₃	100.09	2	2.743
Iron(III) hydroxide	Fe(OH) ₃	106.87	3	3.854
Iron(III) oxide	Fe ₂ O ₃	159.7	6	5.158
Methanesulfonic acid	CH ₃ SO ₃ H	96.10		

Antiprex® E requirements for sulphate and phosphate scales should be determined experimentally.

² The reaction of Antiprex® E with sulfate and phosphate scales is an equilibrium reaction and does not go to completion.

The solubility product, K_{sp} , for the reaction will also be effected by temperature, the presence of common ions and the ionic strength of the solution.

Worked Example

A tails discharge line one kilometre long has built up a layer of scale 1.4 cm thick reducing the cross sectional area of the pipe by nearly eighteen percent. This has resulted in significant reduction in flows through the line. The scale is predominantly calcite with some particulate inclusions from the tails slurry.

Sample Scale data

Pipeline length	1 km = 1,000 m
Pipe diameter (ID)	30 cm = 0.30 m
Thickness of scale	1.4 cm = 0.014 m
Scale composition	80%(w/w) calcite : 20%(w/w) tails
Density of scale	2,710 kg/m ³
Density of Antiprex® E	1.35 g/cm ³ = 1.35 kg/L
MSA content of Antiprex® E	70%(w/w)
Minimum Flow rate	150 m ³ /hr
Formula mass of calcite	100.09 g/mole
Required Contact time	1 hour @ 10% Antiprex® E





$$\text{Total mass of calcite} = \frac{\pi(0.15^2 - 0.136^2) \times 1000 \times 2710 \times 80}{1 \times 100} \frac{\text{ratio} \times \text{m}^2 \times \text{m} \times \text{kg} \times \text{ratio}}{\text{m}^3 \times \text{ratio}}$$

$$= 27271.13 \text{ kg (Eq : 6)}$$

$$\text{Mass of Antiprex}^\circ \text{ E required} = 27271.13 \times 2.743$$

$$= 74,804 \text{ kg (Table : 1)}$$

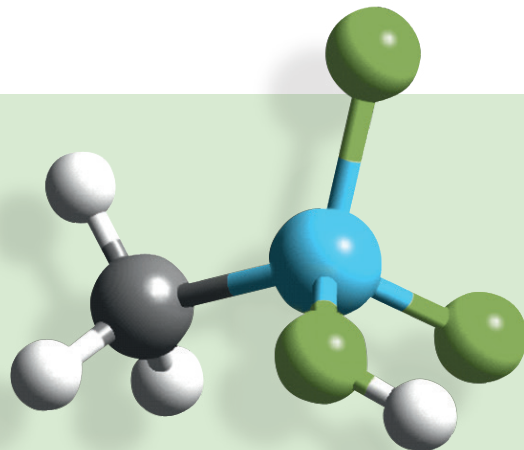
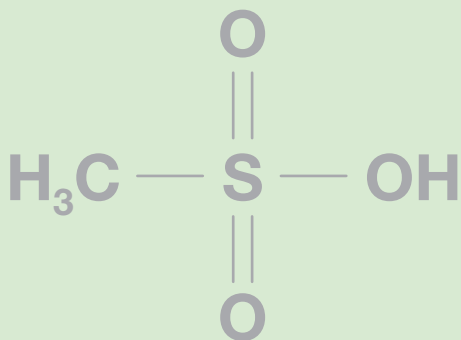
$$\text{Solution volume for required contact time} = 150 \text{ m}^3 \text{ (Eq : 7)}$$

$$\text{Volume of 10\% Antiprex}^\circ \text{ E solution required} = \frac{74,804 \times 1 \times 70 \times 1}{1.35 \times 10 \times 1000} \frac{\text{kg} \times \text{L} \times \% \times \text{m}^3}{\text{kg} \times \% \times \text{L}}$$

$$= 387.87 \text{ m}^3$$

In this instance, the volume of Antiprex[®] E solution is more than adequate to achieve the desired one hour contact time. It may be appropriate to split the cleaning into two or more slugs of

acid solution to reduce the total mass of carbon dioxide liberated at one time. If the scale is acid resistant the concentration of the acid might be increased to accelerate dissolution of the scale.



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