



ENVIRONMENTAL COMPATIBLE SCALE INHIBITOR FOR THE MINING INDUSTRY

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ABSTRACT

The formation of barium sulfate scale is one of the major challenges of the drainage of coal mines, as barium containing pit water is mixed with sulfate containing water before being pumped aboveground. Traditionally this has been overcome by the addition of scale inhibitors based on phosphonic acids. However, due to the enforcing legislation there is a need for a scale inhibitor with improved ecological behaviour. A new scale inhibitor based on polyaspartic acid is as safe and effective as conventional phosphorous containing inhibitors, but has a much higher environmental compatibility. Results of a three year field trial are presented.

Keywords: barium sulfate, calcium carbonate, scale inhibitor, polyaspartic acid, phosphonic acids, coal mine, pit water; pump, water raising

INTRODUCTION

Mining operations extract more than just mineral resources such as coal and ores. Also there is a huge amount of pit water, which has to be pumped aboveground. The water comes from different levels and varies significantly in composition, as it passes different geological formations. Table 1 shows the water composition of two veins of the same pit. This drainage water is collected and mixed underground before being pumped aboveground. Thereby, the solubility of poorly soluble salts can be exceeded, thus causing precipitation.

Due to the very low solubility of barium sulfate, that has a solubility product of $1.05 \cdot 10^{-10} \text{ mol}^2/\text{l}^2$, a precipitate is formed in almost any case, where barium containing water is mixed with sulfate containing water. Besides this, also precipitation of strontium sulfate and calcium carbonate can occur in the drainage water. Since their solubility products are considerably higher than barium sulfate (strontium sulfate $3.42 \cdot 10^{-7}$

mol^2/l^2 ; calcium carbonate: $4.95 \cdot 10^{-9} \text{ mol}^2/\text{l}^2$), these solids only form in pit water to a minor extent or under special conditions.

These precipitates cause serious problems, as they all tend to form very hard scale. Especially barium sulfate scale is very difficult to remove. In practice this has to be done by mechanical means. Indeed, the formation of barium sulfate scale in pipes and water raising pumps is one major problem of the drainage of coal mines in Germany. Table 2 shows the analysis of scales from two different mines. Thus, if no measures are taken against the formation of barium sulfate, frequent maintenance of the water raising pumps and even an exchange of the rising mains can be the consequences. Disassembling of pipes and pumps and installing new ones underground is a very time-consuming process. At the same time high expenditure is connected therewith.

By the addition of scale inhibitors to the pit water the formation of barium sulfate precipitates and scale formation can be avoided. For more than 15 years this has been general practice in those mines that had to raise barium containing pit water. These inhibitors are, however, pumped aboveground together with the pit water and are discharged without further treatment into surface waters. Consequently, only inhibitors with a low aquatic toxicity could be used to prevent any detrimental effect on the aquatic community of life. Therefore, approvals for chemicals added to the pit water by both the mining authority and the local water authority are necessary, to ensure that only chemicals are used, that are in accordance with this requirement.

For the purpose of barium sulfate inhibition products based on phosphonic acids are widely used. They are distinguished by a good efficacy and a considerably low aquatic and human toxicity. Furthermore, their ecological behaviour is well-known, as it has been subject to intensive research for many years¹⁻⁷. Recently, general risk assessments of some phosphonic acids proved, that they represent no risk for the environment^{8,9}. However, their poor biodegradability and the phosphorous content can make them an unacceptable burden on the environment. The raised water is discharged into surface waters that often are used as drinking water reservoirs or that are only small running waters. Therefore, the regulations about the use of scale inhibitors in the mining industry are getting more and more stringent. Finally, there is a demand for an efficient scale inhibitor with a clearly improved environmental compatibility.

The product profile of the new 'green' scale inhibitor was set up and consists the following requirements:

- Excellent barium sulfate scale inhibition
- Satisfying calcium carbonate scale inhibition
- Low aquatic and human toxicity

- High biodegradability (readily biodegradable according to OECD 301)
- pH above 6.5 ⁽¹⁾
- Not subject to labelling
- Low water hazard class
- Good price/performance ratio
- Free of phosphorous content

Currently none of the state of the art scale inhibitors fulfills all of these demands. Therefore, a new scale inhibitor has been developed to fill this gap.

EXPERIMENTAL

The screening of new scale inhibitors was carried out in comparison to the standard phosphonic acid based product as the reference with regard to scale inhibition of barium sulfate and calcium carbonate. The new scale inhibitor should provide at least a comparable barium sulfate stabilization, whereas a somewhat lower level of inhibition of calcium carbonate scale was accepted. The demand of 'readily biodegradable' cannot be met by any of the conventional phosphonic acids, polyacrylic polymers and copolymers available. Therefore, the investigations were focused on two new kind of chemicals with superior biodegradability, that had been developed recently.

Mono carboxylated starch

This chemical is produced from starch by oxidation with oxygen, where nitrogen dioxide reacts with the starch molecule to form nitrogen monoxide and mono carboxylic starch. The nitrogen monoxide is recycled into the process by oxidation with oxygen. By variation of the conditions of preparation the properties of the final product can be adjusted. Details of the production process and the application of mono carboxylic starch as a scale inhibitor have been reported in the literature ¹⁰⁻¹². The chemical structure of monocarboxylic starch is shown in figure 1a.

Polyaspartic acid

Polyaspartic acids have been well-known for many years. However, in spite of their remarkable properties for a long time they were only of scientific interest because they were not commercially available in larger quantities. Today, there are three main methods for industrial production of polyaspartic acid:

- solid-phase thermal condensation of aspartic acid ¹³
- catalyzed polymerisation of aspartic acid ¹⁴
- reaction of maleic acid with ammonia ¹⁵.

⁽¹⁾ Any formation of hydrogen gas underground must be excluded, even in case of an accident.

In any case polysuccinimide forms as an intermediate, that is converted to polyaspartic acid by alkaline hydrolysis. Figure 1b shows the principal chemical structure. The structure and properties of polyaspartic acid, that considerably vary in dependence of the reaction path, have been subject to intensive research ¹⁶⁻¹⁸. Mainly the mean molecular weight, the distribution of molecular weights, the formation of branched structures as well as purity are effected by the production path.

Various applications of polyaspartic acid as scale inhibitor against calcium sulfate, barium sulfate and calcium carbonate, as a dispersant as well as a corrosion inhibitor give an impression of the versatility of this group of chemicals ¹⁹⁻²². However, until now there have been no cases, where polyaspartic acid was really successfully used in the field.

Screening tests

Inhibition of barium sulfate precipitation was tested in a standard static bottle test. The composition of the test solution is given in table 3. To stress the inhibitors different amounts of iron were added to the test solutions.

Evaluation of dynamic calcium scale inhibition was conducted in a test apparatus shown in figure 2 using quite harsh conditions with a calcium level of 5.4 mol/m³, a magnesium level of 1.8 mol/m³ and a total alkalinity of 20 mol/m³. Over a two hour period the test solution was pumped at a constant flow rate through a helical glas tube heated from outside up to 80 °C. The calcium carbonate precipitation was removed with a defined quantity of hydrochloric acid and the calcium level in the acidic solution was determined. Comparison against a blind sample provided the percentual calcium carbonate inhibition of the compound.

RESULTS

Screening

Preliminary studies were carried out with different types of monocarboxylic starches prepared at Henkel KGaA, Duesseldorf and thermally condensed polyaspartates from Donlar Corporation, Bedford Park. Table 4 lists the evaluated inhibitors. Eventually, it became apparent that only polyaspartates provide as good barium sulfate inhibiton as the phosphonate based formulation P3-ferrofos[®] 514 ⁽¹⁾ (PHOS) used at the mining industry (figure 3).

However, PHOS proved to be a more efficient calcium carbonate inhibitor as polyaspartic acid. Variation of molecular weight clearly improved efficacy (figure 4), but could not

⁽¹⁾ P3-ferrofos[®] is a registered trade-mark of the Henkel KGaA, Germany

fully meet the standard defined by PHOS. As shown in Figure 5 also with polyaspartic acid a complete calcium carbonate inhibition could be achieved. Therefore, sufficient calcium carbonate inhibition should be expected with regard to the conditions of the pit water.

Final Assessment

The final assessment of the new polyaspartic acid based product P3-ferrofos[®] 8413-3 (PASP) versus the phosphonate containing product (PHOS) is illustrated in figures 6 to 8. Calcium carbonate inhibition of PASP at higher concentration is comparable to PHOS (figure 6). PASP gives at least the same barium sulfate inhibition as PHOS at 70 °C (figure 7), whereas PASP is even more efficient at lower temperature (figure 8). The evaluations were conducted at stressed conditions with an iron level of 2 g/m³ in the test solution.

Pit water studies

In addition to the screening test using a standardized water quality, further experiments utilized water samples taken from two main veins of the water drainage of a coal mine (table 5). Barium sulfate inhibition tests were carried out analogously to the screening tests. The mixing ratio of the samples was adjusted to the ratio of volume flow of the veins, that is approximately 1 to 6. Without addition of any scale inhibitor barium was almost quantitatively precipitated as barium sulfate. The addition of both PHOS and PASP could provide complete barium sulfate stabilization. However, a lower amount of PASP was needed to achieve this (figure 9).

Storage stability

Rapid degradation of the molecule in surface waters is one of the benefits of PASP versus PHOS. Rapid loss of activity already during storage of the chemical, however, would be unacceptable. Therefore, the long term storage stability of PASP was tested taking into account the elevated temperature in a mine underground. During a six month period a PASP sample was stored at 40 °C and the barium sulfate inhibition was tested several times. The results (figure 10) clearly indicate that PASP retains its efficiency under these conditions.

Ecological and toxicological evaluation

Both phosphonates and polyaspartates have been subject to extensive ecological and toxicological investigations. Table 6 shows a synopsis of the most important data and the classifications according to the chemical law and German water hazard class for PHOS and PASP. The most important benefits of PASP are:

- excellent biodegradability
- zero phosphorous content

- water pollutant class zero in terms of German classification, the least dangerous category

FIELD TRIAL

Prior to any practical test at a German coal mine the product had to pass several approval procedures to ensure no impact on the people handling the product or on the environment, mainly the brook or river the pit water is fed into. Finally, in 1994 the mining authority and the water authority had licensed the new product for a first field trial.

The coal mine is located in the East of the Ruhrgebiet in Germany. It was founded in 1902 and today produces between 9,000 and 10,000 tons of hard coal per day. Approximately 3,500 people are employed aboveground and underground. The maximum depth of the streaks is 1,100 m and the main water raising is located 970 m underground. Each day 6,000 m³ of pit water are pumped above group by three water raising pumps. A single pump costs 400,000 to 500,000 DM (250,000 to 300,000 \$).

In the past, this coal mine had suffered serious barium sulfate scaling in the water mains and the raising pumps due to barium containing water (table 7). In extreme cases the raising pumps could be run only for a few hundred hours without significant loss of pumping capacity. About 15 years ago the addition of a scale inhibitor (PHOS) to the pit water had been successfully introduced. By the addition of 4 g/m³ of PHOS with reference to the total drainage water formation of barium scale could be prevented. The product was added into the barium containing vein prior to the pumping sump. So, the operating time of the raising pumps was improved to 8,000 hours on the average without any maintenance.

In spite of the high efficiency and low toxicity of PHOS the water authority began to put pressure on the responsible people of the coal mine to substitute it by a more environmental friendly product. As the pit water was discharged into a small river there was a serious concern because of the poor biodegradability and the eutrophic potential of PHOS. Therefore, a field trial with the polyaspartic acid based product was started March 1994. First a modification ⁽¹⁾ (PASP*) was put into operation until November 1994, when dosage was finally switched to PASP. Dosage of PASP* and PASP was on the same level as PHOS, i. e. 4 g/m³ of pit water. Furthermore, the position of inhibitor dosing remained unchanged.

⁽¹⁾ PASP* still contained some phosphorous. Due to the use of a polyaspartate with improved efficiency, PASP now is phosphorous free.

The trial was controlled mainly by regular water analysis and inspections of the raising pumps. Any significant increase of operational pressure or any serious irregularity in the operational behaviour of the pump would have been judged as failure and would have terminated the trial. The target was to achieve 8,000 hours of operation before the next main revision of the pump. Due to the alternate use of the three main raising pumps the trial lasted from March 1994 until May 1997, when two pumps had finally reached more than 9,000 hours of operation. During this time these pumps had been lifting drainage water treated by three different products (figure 11). However, in any case a poor barium sulfate inhibition would have proven very shortly by a fast decrease in pumping capacity. Therefore, the trial was unanimously judged as successful. As a consequence, the management has decided to replace the phosphonate based product completely by PASP.

A second field trial with PASP had been started in November 1994 at a coal mine in the west of the Ruhrgebiet. Also in this case PASP had replaced PHOS. Until now it is running without any problems. However, the raising pumps have not yet achieved the overall operational time that had been set as a target. Therefore, the trial cannot definitely be judged.

CONCLUSIONS

A new scale inhibitor based on polyaspartic acid has been developed for applications in the mining industry. It combines excellent barium sulfate inhibition with satisfying calcium carbonate inhibition. It is readily biodegradable, contains no phosphorous and is assigned to the least dangerous category of water pollutants according to the German classification. This coupled with a low aquatic and human toxicity allows it to be used in applications where conventional scale control additives are facing problems with environmental compatibility.

The new polyaspartate scale inhibitor has been tested in a three year field trial at a German coal mine. It is providing at least the same efficiency as the traditional scale inhibitor and now has successfully substituted the previously used product containing phosphonates.

ACKNOWLEDGEMENTS

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TABLE 1
ANALYSIS OF TYPICAL PIT WATER VEINS

<i>Parameter</i>	<i>Vein A</i>	<i>Vein B</i>	
pH	7.3	7.1	
Total Alkalinity	3.2	3.9	mol/m ³
Total Hardness	31.5	77.3	mol/m ³
Calcium	26.0	51.3	mol/m ³
Chloride	10.1	35.3	kg/m ³
Total Iron	0.2	0.3	g/m ³
Sulfate	299.5	< 10	g/m ³
Barium	< 1	100.2	g/m ³
Suspended Solids	45.7	95.3	g/m ³

TABLE 2
ANALYSIS OF SCALE IN RAISING PUMPS

<i>Parameter</i>	<i>Pump A</i>	<i>Pump B</i>	
Loss of ignition (500 °C)	1.1	1.2	%
Loss of ignition (800 °C)	0.9	2.4	%
SiO ₂	1.0	< 0.1	%
Al ₂ O ₃	0.9	0.4	%
CaO	1.4	1.5	%
Fe ₂ O ₃	0.3	0.3	%
BaO	55.9	53.0	%
SO ₄	38.2	39.0	%

TABLE 3
COMPOSITION OF BARIUM SULFATE INHIBITION TEST WATER

<i>Parameter</i>	<i>Value</i>	
Sodium	26.9	kg/m ³
Potassium	1.02	kg/m ³
Calcium	8.85	mol/m ³
Magnesium	13	mol/m ³
Bicarbonate	43	mol/m ³
Barium	687	g/m ³
Sulfate	270	g/m ³
Chloride	42.5	kg/m ³

TABLE 4
DESCRIPTION OF SCALE INHIBITORS EVALUATED

<i>Inhibitor</i>	<i>Chemical Description</i>	<i>Solid Matter [%]</i>	<i>Acid Number</i>	<i>Molecular Weight [g/mol]</i>
Mcs1	Monocarboxylated Starch	93	395	n.d.
Mcs2	Monocarboxylated Starch	91.5	300	n.d.
Pasp1	Polyaspartate	42	n.d.	4500
Pasp2	Polyaspartate	47	n.d.	4000
PHOS	Phosphonates	40	n.d.	

TABLE 5
ANALYSIS OF PIT WATER FOR BARIUM SULFATE INHIBITION TEST

<i>Parameter</i>	<i>Barium Vein</i>	<i>Sulfate Vein</i>	
pH	7.3	7.2	
Total Alkalinity	10.5	5.0	mol/m ³
Total Hardness	36.9	9.5	mol/m ³
Calcium	24.3	6.3	mol/m ³
Chloride	18.5	5.2	kg/m ³
Total Iron	n.d.	n.d.	g/m ³
Sulfate	< 10	250	g/m ³
Barium ⁽¹⁾	200	< 1	g/m ³
Suspended Solids	73	15	g/m ³

⁽¹⁾ Barium level was raised from 166 to 200 g/m³ by addition of Barium chloride

TABLE 6
SYNOPSIS OF ECOLOGICAL AND TOXICOLOGICAL DATA

	<i>Method/Regulation</i>	<i>PASP</i>	<i>PHOS</i>
pH (1% solution)		9.9	5.2 ⁽¹⁾
Labelling	Chemical law	none	none
Water Pollutant Category ⁽²⁾	German classification	0	1
PO ₄ -content		0 %	20 %
Biodegradability	OECD 302 B	> 80 % (28 d)	n. d.
	OECD 301 B/F	> 60 % (28 d) ⁽³⁾	n. d.
	OECD 301 D/E ⁾	n. d.	< 30 %
Aquatic Toxicity			
• Fish	DIN 38 412 T 15	EC 50: > 1,000 mg/l	EC 50: > 500 mg/l
• Daphnia	DIN 38 412 T 11	EC 50: > 1,000 mg/l	EC 50: > 500 mg/l
• Bacteria	DIN 38 412 T 27	EC 50: > 1,000 mg/l	EC 50: > 1,000 mg/l
• Algae	DIN 38 412 T 9	NOEC: > 100 mg/l	EC 50: > 1,000 mg/l

⁽¹⁾ The requirement of a pH > 6.5 was set up after the first approval for PHOS.

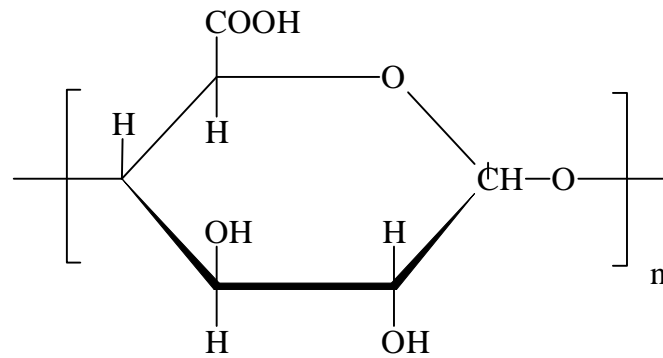
⁽²⁾ 0 is the lowest category and 3 is the highest category of water pollutant

⁽³⁾ Readily biodegradable according to the OECD classification

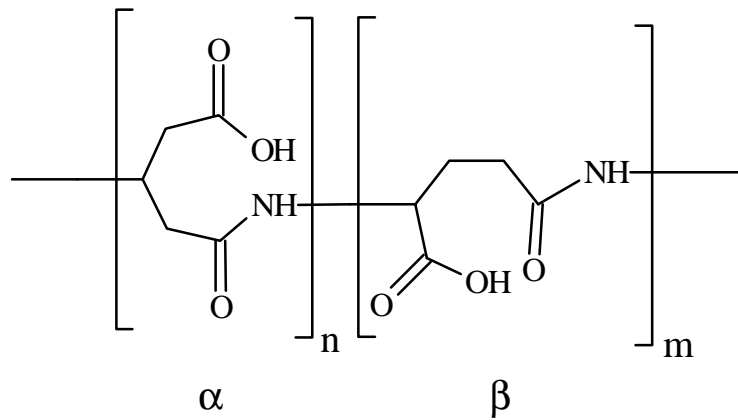
TABLE 7
VARIATION OF COMPOSITION OF PIT WATER DURING FIELD TRIAL

<i>Parameter</i>	<i>Barium Vein</i>	<i>Sulfate Vein</i>	
pH	6.4 - 7.6	7.2 - 7.7	
Total Alkalinity	2.0 - 2.6	2.0 - 2.1	mol/m ³
Total Hardness	65 - 130	19 - 91	mol/m ³
Calcium	44 - 85	13 - 60	mol/m ³
Chloride	24.2 - 58.2	7.9 - 39.1	kg/m ³
Total Iron	0.3 - 2.4	0.1 - 1.8	g/m ³
Sulfate	< 10 - (23)	(< 10) - 45	g/m ³
Barium	123 - 165	< 1 - 19 (181)	g/m ³
Suspended Solids	44 - 72 (505)	86 - 170	g/m ³

The numbers in parentheses represent extrem values that have only been measured once.



a) Monocarboxylated starch



b) Polyaspartic acid

FIGURE 1 - Chemical structure of biodegradable scale inhibitors

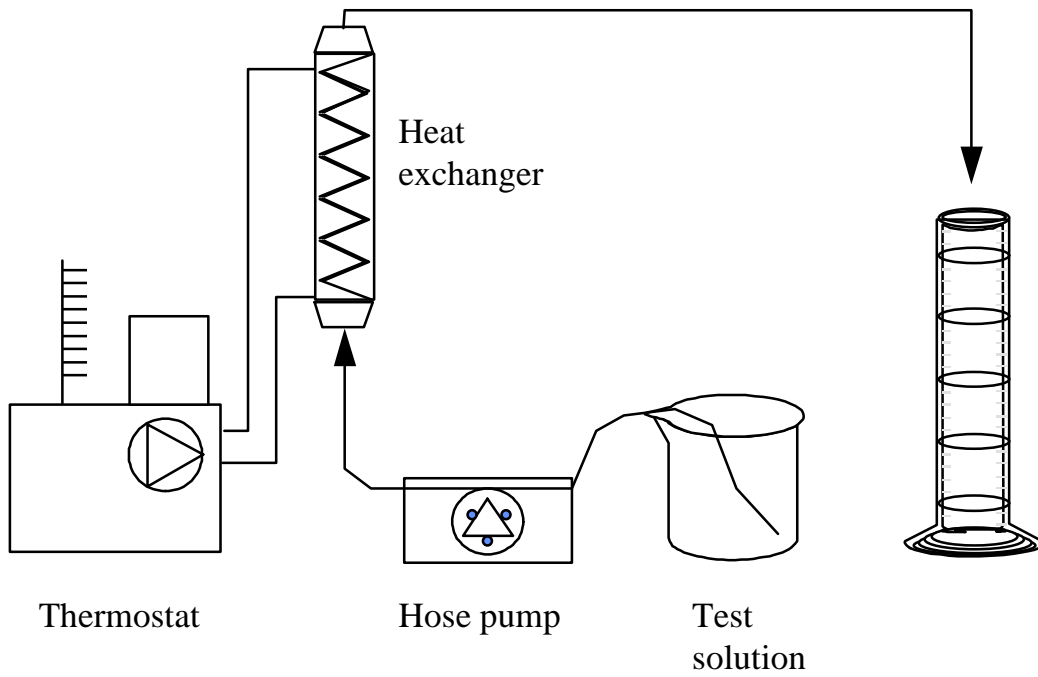


FIGURE 2 - Scheme of the calcium carbonate scale inhibition test apparatus

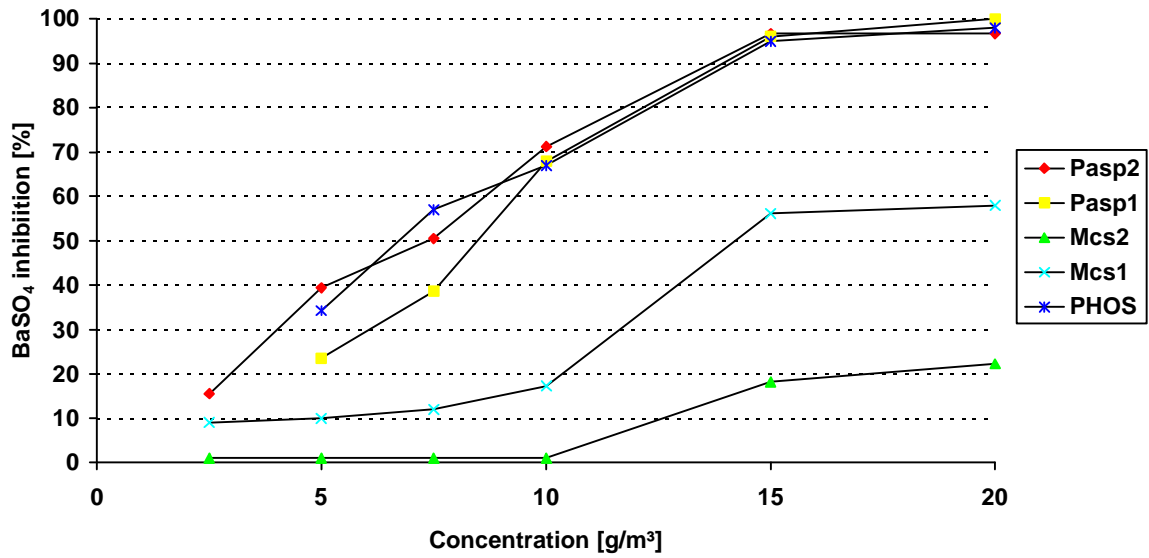


FIGURE 3 - Barium sulfate inhibition in test water in dependence of inhibitor concentration, 70 °C, 3 hours

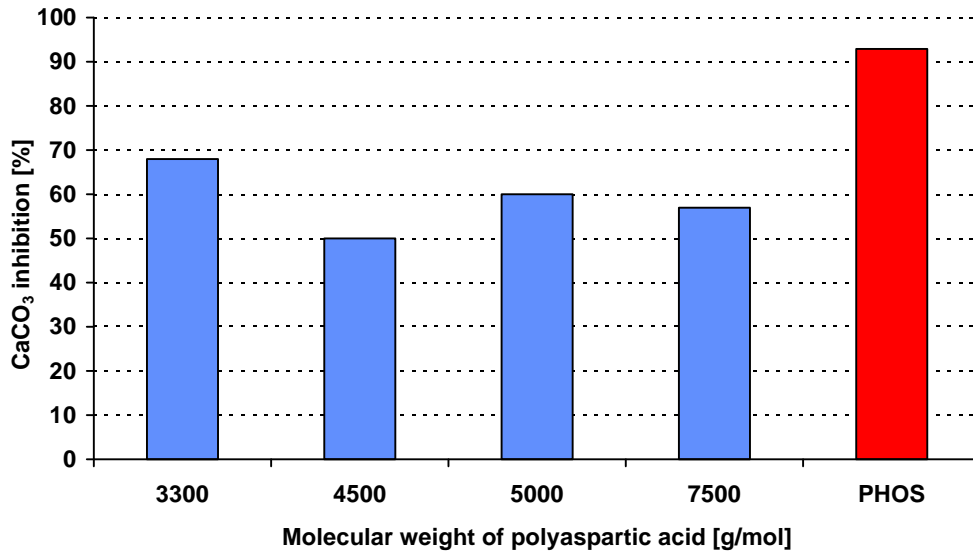


FIGURE 4 - Dependence of calcium carbonate inhibition of polyaspartates at a concentration of 2 g/m³ on the molecular weight. The result for PHOS is shown for comparison.

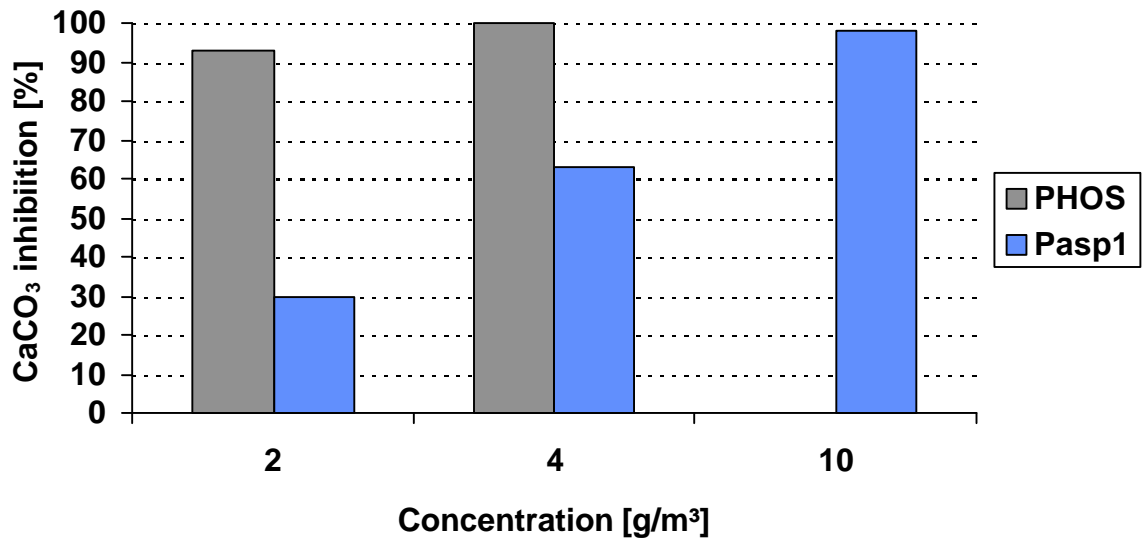


FIGURE 5 - Calcium carbonate inhibition of polyaspartic acid (Pasp1) versus phosphonates (PHOS) in dependence of concentration.

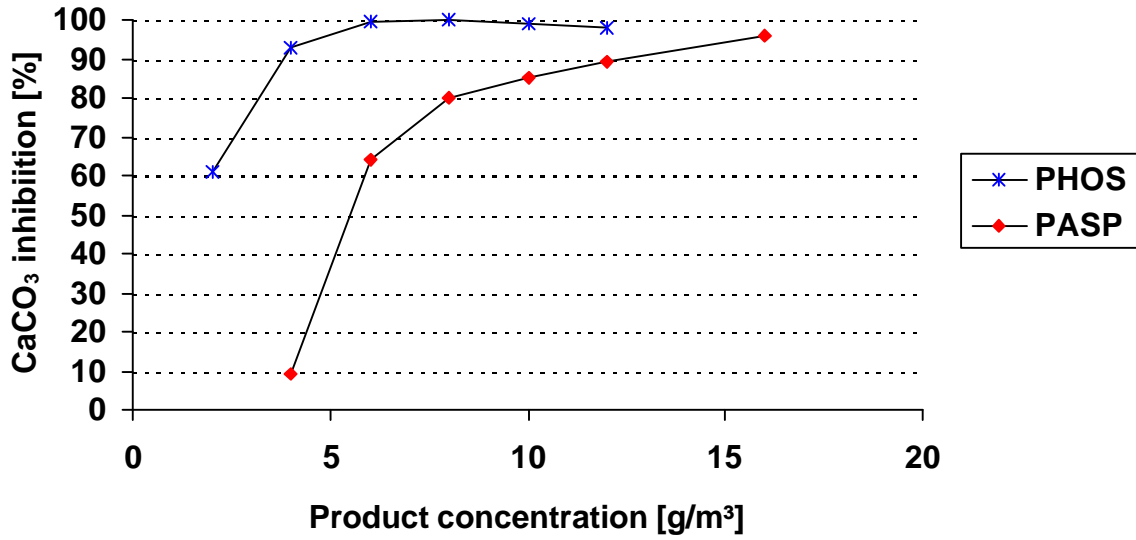


FIGURE 6 - Calcium carbonate scale inhibition of products PHOS versus PASP in dependence of concentration

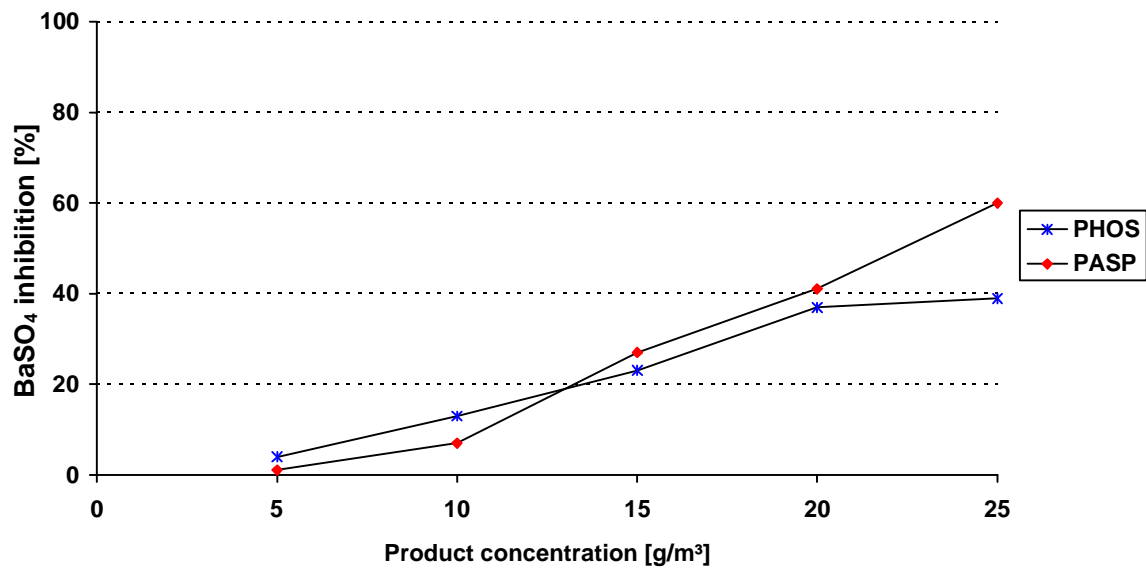


FIGURE 7 - Barium sulfate inhibition in test water of products PHOS and PASP in dependence of concentration at 70 °C. The test solutions contained 2 g/m³ Fe.

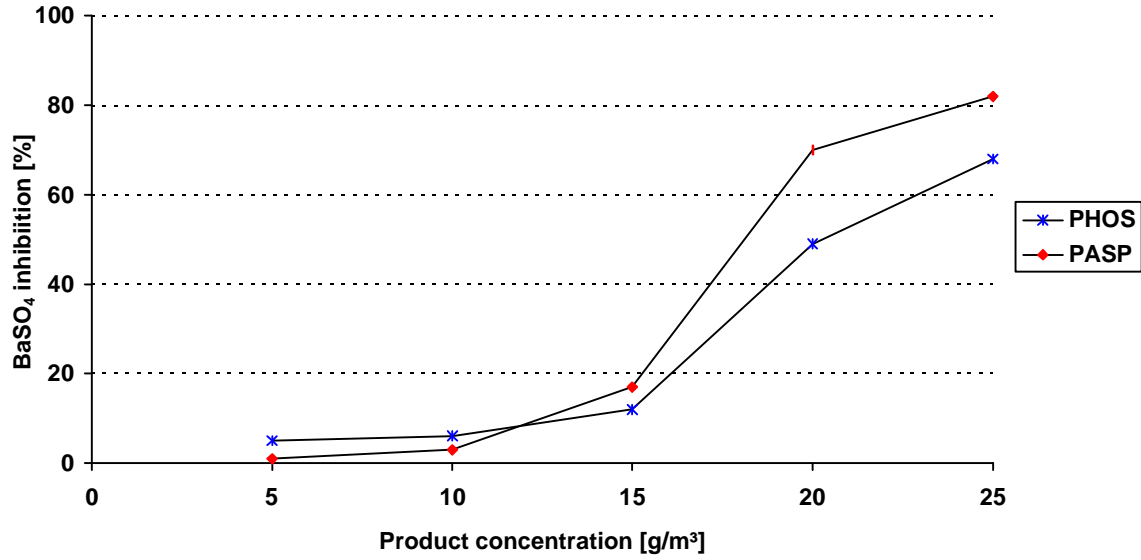


FIGURE 8 - Barium sulfate inhibition in test water of products PHOS and PASP in dependence of concentration at 30 °C. The test solutions contained 2 g/m³ Fe.

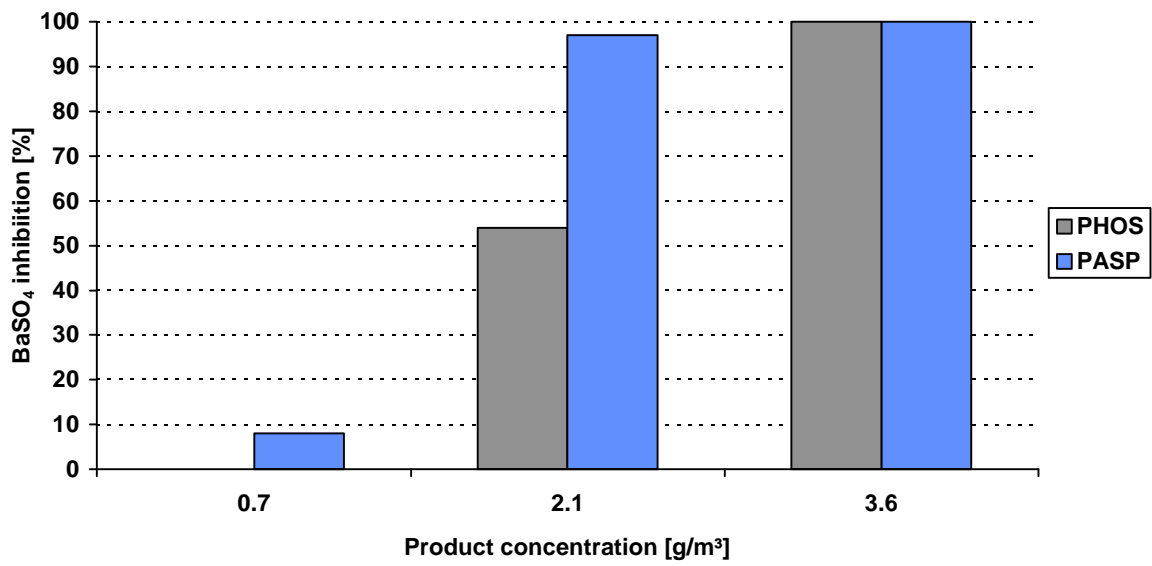


FIGURE 9 - Barium sulfate inhibition in pit water of PASP versus PHOS in dependence of product concentration with reference on the total volume of drainage water.

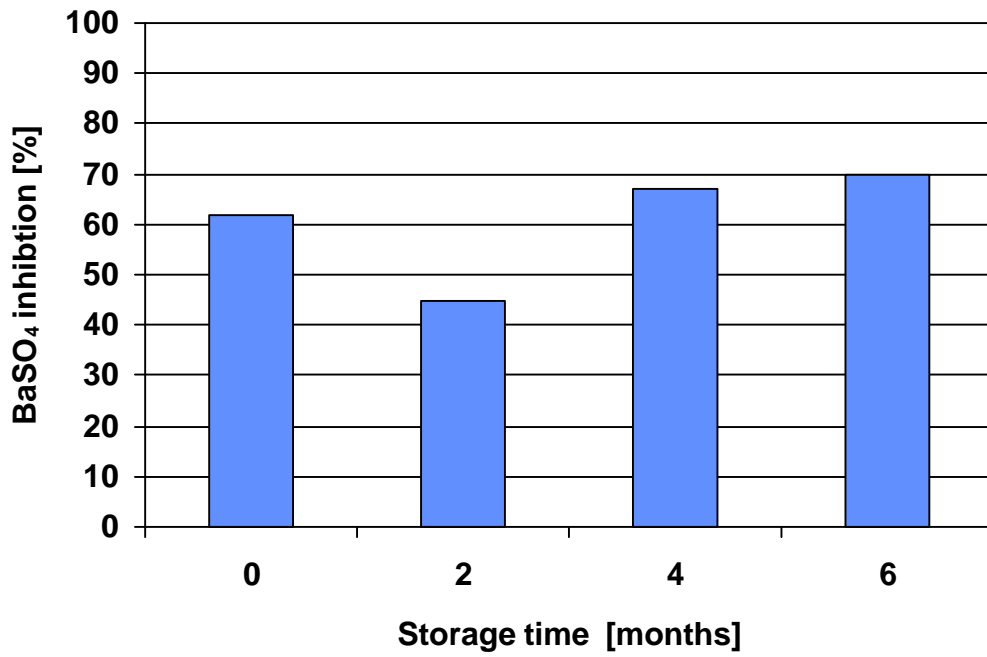


FIGURE 10 - Dependence of barium sulfate inhibition of PASP on storage time at 40 °C.

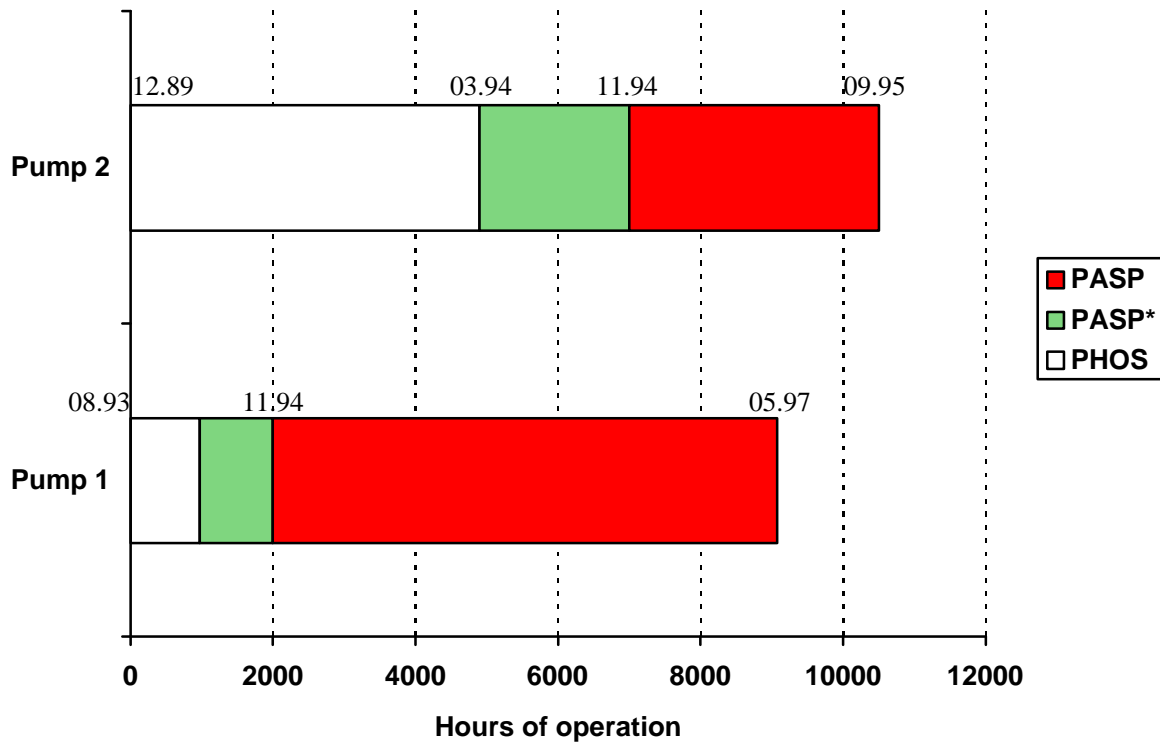


FIGURE 11 - Hours of operations of two main water raisage pumps treated with different barium sulfate inhibitors at a German coal mine. The dosage was 4 g/m³ total drainage water.