

Jiří VIDLÁŘ *, Ctirad SCHEJBAL **, Peter FEČKO ***

ECOLOGICALLY ADVANTAGEOUS METHOD OF SULPHATE MINE WATER CLEANING

EKOLOGICKÁ METODA DESULFATAČE SÍRANOVÝCH DŮLNÍCH VOD

Abstract

By the present paper a characteristics of mine water produced by mining of subbituminous and bituminous coal as well as by mining of gypsum from the point of view of hydrogeology and water management is given. Principal possibilities of desulphation of such mine water by physical-chemical procedures and chemical precipitation are discussed. Development of ecologically favorable method of chemical precipitation of sulphates and its verification are described. An orienting proposal of handling of water treatment plant sludge is mentioned.

Abstakt

Článek uvádí hydrogeologické a hydrochemické charakteristiky důlních vod z těžby hnědého uhlí, resp. sádrovce. V návaznosti je dále uveden princip metody desulfatace těchto vod originální metodou, vyvinutou na řešitelském pracovišti. Podstatou této metody je chemické srážení síranů kombinací vnesených iontů vápníku a hliníku v silně alkalickém prostředí. Vzniklá sraženina síranu hlinitovápennatého (ettringitu) může být technologicky využita nebo likvidována ekologicky přijatelným způsobem. Metoda desulfatace byla vyvinuta za finanční podpory Grantové agentury ČR.

Key words: coal mining mine water, gypsum opencast mine water, mine water sulphate, desulphation, chemical precipitation of sulphates, waste water sludge.

Introduction

Problematics of mine water and other waste water with higher content of sulphates is coming ever more to the fore of interest of water management and state inspection bodies, because technological or waste water represent frequently enormous quantities of noxious substances encumbering recipients and natural ecological systems.

Specialised workplace of Mining Geological Faculty of VŠB-Technical University of Ostrava (Institute of Environmental Engineering – IEI HGF) has dealt with research of potential procedures and development of desulphation technology already since 1994. Solving of problems concerned was motivated by requirements of mine companies provoked by tightening up of emission limits for sulphate content in waste or surface water due to ordinance N^o 82/99 of Czech government or eventually due to cancelling of hitherto valid water management exemptions.

By financial support of Grant Agency of Czech Republic and of several mine companies the designer workplace was enabled to enhance further its research work so as to reach a form of verified project of original technological procedure of mine water desulphation based on chemical precipitation of sulphates including co-precipitating of some other concomitant ions.

* Prof. Ing., CSc., VŠB-TU Ostrava, Hornicko-geologická fakulta, 17. listopadu 15, 708 33 Ostrava

** Prof. Ing., CSc., VŠB-TU Ostrava, Hornicko-geologická fakulta, 17. listopadu 15, 708 33 Ostrava

*** Prof. Ing., CSc., VŠB-TU Ostrava, Hornicko-geologická fakulta, 17. listopadu 15, 708 33 Ostrava

The desulphation technology of IEI HGF was developed primarily for conditions and requirements of cleaning of mine water produced by mining of coal or gypsum (anhydrite). However, its further modifications will be able to satisfy needs of cleaning of sulphate waste water regardless of its genesis.

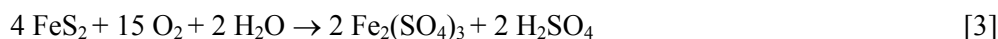
Characteristics of mine water from mining of coal or gypsum (anhydrite)

Mine water pumped from open pit or underground mines are encumbered with increased content of ions of SO_4^{2-} , Fe^{2+} , Fe^{3+} , RL, NL and of acidic pH, above all due to oxidation of iron sulphides (pyrite, marcasite) and due to incorporation of their soluble components into solution /1/.

Oxidation of pyrite was until now still ever explained by traditional chemical diagram of Temple-Delchamps, but more recently catalytic activity of thion bacteria has been taken into account. However, a detailed course of subsequent reactions has not been unequivocally evidenced as yet:



Overall reaction could have the following form:



In view of kinetics the continuation of basic chemical reaction [1] by means of mechanism [2] is very important, because oxidation of Fe^{2+} to Fe^{3+} only by air oxygen is very slow and the rate of total reaction is limited by it.

It results from the above-mentioned that air oxidations alone cannot be practically used for degradation of pyritic sulphur. Therefore, in certain application considerations catalytic action of enzymatic products of specific bacteria is taken into account which help indirectly oxidation of pyrite. Assumed biochemical reactions are based on action of product of bacterial metabolism, i.e. on effect of ferric sulphate – $\text{Fe}_2(\text{SO}_4)_3$ within sulphuric acid medium whereby ferric sulphate is generated by biological oxidation of ferrous sulphate – FeSO_4 by means of culture of *Thiobacillus ferrooxidans*. Oxidation activity of the last-mentioned microorganism is considered by some authors as decisive for rapidity of decomposition of iron disulphides /2/ :



Applicability of the above-mentioned chemical and biochemical reactions in relation to cleaning of water from coal quarries and underground coal mines could be summarised in partial conclusion indicating additive effect of air oxygen, bivalent iron and thion bacteria on total sulphate content of such water.

Mine water from mining of gypsum (anhydrite) contains above-limit concentrations of sulphates as a consequence of solubility of such minerals.

Characteristics of mine water from mining brown (subbituminous) coal

Mining of brown coal in Czech Republic is concentrated in coal production centres of coal basins in North-West Bohemia. Hydrogeological condition of are very different in particular areas. Ground water belongs on the one hand to an active water exchange zone and on the other hand to a deeper zone with slower water movement. Low mineralised water of active water exchange zone possesses a Ca-hydrogencarbonate nature. In the measure of brown coal seams water of Ca-sulphate type with total mineralisation of up to several g.l^{-1} occurs /7/. Occurrence of sulphate ions in such mine water oscillates within range of 500 to 3500 mg.l^{-1} /1/.

In view of surface water protection against pollution in accordance with applicable laws and regulations it is necessary to treat it prior to discharge of such water into recipients, i.e. to neutralize it, to remove iron from it, to separate undissolved substances and to desulphate. The first three cleaning degrees are rela-

tively easy and they are applied commonly by mine water treatment plants. Desulphation processes are technically and technologically more demanding and therefore they do not belong until now among common established technologies.

Admissible concentration of sulphates in surface water is stipulated to be 300 mg.l^{-1} by government ordinance N°82/99 Sb. (emission limit value). This value is limit value also for discharged mine water (emission limit value).

Characteristics of mine water from hard coal mining

Bituminous hard coal with higher sulphur content occurs in Lower Silesian Coal Basin. The biggest problem is represented by mine fields of Kateřina Colliery in vicinity of Trutnov. Its coal-bearing Permian-Carboniferous is part of northwestern wing of extensive complicated brachysyncline extended in NW-SE direction /8/. The coal seam measure of 100-150 m thickness is constituted by grey mudstones, siltstones and fine-grained sandstones. It encompasses up to 10 inclined coal seams, out of which 6 coal seams are worked by Kateřina Colliery.

Hydrogeological conditions are determined essentially by active circulation of subsurface water as Carboniferous rocks have a very low permeability. The nature of mine water is affected by relatively varied sulphidic mineralisation and in some parts also by uranium mineralisation and mineral components released from burning spoil heap. The mixed mine water which must be cleaned, contains $1500\text{-}2000 \text{ mg.l}^{-1}$ sulphate ions.

Characteristics of mine water from mining of gypsum

The only actually exploited gypsum deposit of Czech Republic is located in northeastern part of the Republic and it is a part of Opava basin belonging to Neogen Carpathian Depression bordering the external arch of Carpathians. Gypsum horizon is developed in a measure of calcareous illitic and illitic-montmorillonite clays within total scope of basin with three genetic types, i.e. fibrous gypsum, laminated microcrystalline gypsum and massive gypsum. The Kobeřice gypsum deposit is excavated by open pit of 90 ha surface with 60 m super-elevation. All genetic types of gypsum are exploited.

The locality is featured as an object with difficult hydrogeological conditions and occurrence of two aquifers. The upper Quaternary aquifer is located in basal position of glacial sediments and it is featured by free groundwater level and active water circulation. Its chemistry corresponds to type Ca-HCO_3 with low mineralisation. Thus fresh water is concerned the quality of which is equal to potable water. The lower Tertiary aquifer is bound with deposit filling of gypsum rocks and it is featured by pressurized water level and slow water exchange. Its chemistry corresponds to Ca-SO_4 type with sulphate content of $1500\text{-}2000 \text{ mg.l}^{-1}$, thus saline water is concerned. The Tertiary aquifer is fed locally from Quaternary aquifer.

Potential possibilities of desulphation of mine water

Technological procedures for elimination of sulphates from waste water can be structured as follows:

1. physical-chemical procedures,
2. biological procedures,
3. chemical precipitation procedures.

Into the group of physical-chemical procedures above all *membrane processes* can be classified, i.e. diffusion processes in which for separating of components (ions, molecules) selective permeability of homogeneous or heterogeneous ion-exchange membranes is used. They are technologically highly developed processes, commonly used by modern water treatment technologies for special purposes (military purposes, civil defence and protection purposes etc.). Among them above all reverse osmosis, electrodialysis and ultrafiltration can be ranked. In Czech Republic the membrane processes have not been applied until now for common water treatment or water cleaning due to economic reasons. Into the same group processes of distillation, freezing out and separating by ion exchangers can be further classified. Thermal processes are highly energy demanding and their application for separating of sulphates from mine water is obviously unrealistic.

Water treatment by means of ion exchangers is used in common for concentrating metals from technological solutions, its application for separating sulphates from mine water would require further expensive technologic operations connected with regenerating of ion exchanger and disposal of saline product.

Biological procedures are based on potential capability of *desulphation bacteriae* to reduce sulphates to insoluble sulphides which can be removed mechanically from waste water /3/. They are principally more recent methods featured by low operational cost and unpretentious attendance. A source of energy for specific bacteriae shall be an adequate organic substratum enhancing the BSK₅ index and the technology requires therefore a conventional finishing stage of biological recleaning. In addition to this the desulphation bacteriae require maintaining of optimum water temperature – about 35°C and a very long reaction time.

For the given purpose of desulphation of mine water the following pure bacterial cultures were tested orientingly *Desulfovibrio desulfuricans*, *Desulfovibrio vulgaris*.

It resulted from such orienting experiments that application of selected bacterial cultures during an about 100 hours activity will remove only 25% of sulphates from mine water which cannot be considered as an acceptable result. From the pure research point of view a long-term study of adaptability of the above-mentioned bacterial cultures to the high sulphate content values of mine water would be interesting /5/.

A development of adaptable bacteriae would require a transformation to plasmides of genetic properties of cell on which action of extreme saline sulphate water for a several years period is assumed.

Chemical procedures

Chemical procedures have become subject of our present research /4,5,6/. With regard to possibilities of practical application of potential technology, to ecological issues as well as to economy of water desulphating by water treatment process the processes based on chemical precipitation of sulphates were preferred.

Precipitating should be a controlled process so as to safeguard reliably a necessary reduction of sulphate content and at the same to prevent that the cleaned water would be unnecessarily encumbered by ions of precipitating agent which could contribute to increase of salinity of such water. Substantial part of our study of chemical precipitating of sulphates were reactions of these SO₄²⁻ anions with selected cations of metals forming together with sulphates low soluble and ecologically acceptable compounds.

Within frame of extensive research reducing of sulphates by cations – Ba²⁺, Ca²⁺ was studied separately, while analytically known agent – *barium chloride* BaCl₂ was „standard,,.

Precipitating of sulphates to *barium sulphate* is a process well-known in analytic chemistry where it was used for water treatment purposes already at the the beginning of last century. Many research studies, but also analytical studies have confirmed high efficiency of precipitating which is regulated by the following equation:



Product of solubility of reaction product [7] is $K_s = 1.35 \cdot 10^{-10}$, i.e. the solubility is approximately 1.7 mg BaSO₄ in 1 dm³ water, i.e. about 1 mg SO₄²⁻ ions in 1 dm³ water. Thus precipitating of sulphates by barium cations can be considered as quantitatively effective. Important partial result of research was the finding that adequate donor of precipitating Ba²⁺ cations can be apart of usually applied compounds equally barium sulphide – BaS. However, at its application it is necessary to take into account eventual development of gaseous H₂S (carbon disulphide) which must be subsequently caught up, for instance by means of chemical adsorption by powder zinc oxide ZnO. Although precipitating of sulphates by means of barium cations is highly efficient, its disadvantages connected with unfavorable ecological effects of superfluous content of Ba²⁺ ions together with relatively high prices of barium compounds cannot be dismissed.

Precipitating of sulphates by Ca²⁺ ions to *calcium sulphate* is only partially efficient, as the solubility of the product – CaSO₄ is about 2000-2500 mg.l⁻¹ and thus residual concentration of sulphates at equilibrium state oscillates about 1500 mg.l⁻¹ which is highly above limit concentration value.

Method of cleaning of sulphate mine water by IEI-HGF method

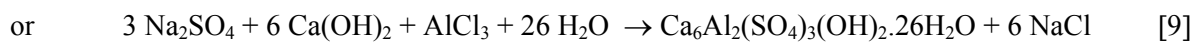
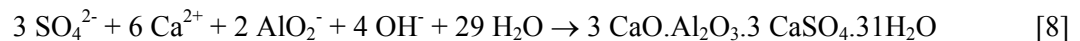
Development of method

The principle of method consists in application of well-known chemical reaction of silicate technology, i.e. capability of cement clinker (calcium aluminosilicate) to bind chemically sulphate anions to low soluble sulphatoaluminates, known as ettringite (Bannister, 1936). This compound is equally known as natural mineral. Transplanting of genetic conditions of ettringite to process of desulphation of sulphate water predicted the research of precipitation of SO_4^{2-} ions by means of combination of Ca^{2+} , OH^- and Al^{3+} ions (or eventually AlO_2^-).

With regard to minimizing of cost and to ecologically most adequate solving of water desulphation our research and development preferred precipitating agents which were efficient and did not introduce any other noxious ions into cleaned water, i.e. calcium hydroxide – $\text{Ca}(\text{OH})_2$ or sodium aluminate – NaAlO_2 , or eventually aluminium chloride – AlCl_3 introducing into process undesirable chlorides, the summarised content of which in water is equally limited.

Chemistry of precipitation reaction

Based on preliminary results the procedure of chemical precipitating using a combination of ions of Ca^{2+} , OH^- , AlO_2^- , or eventually of Al^{3+} ions was selected. From theoretical point of a confirmation of probable course of the following precipitation mechanisms was concerned:



Research work was concentrated above all at finding optimum concentrations of reagents, optimum rate of mixing of reactants and at time course of precipitation reactions. Functional dependence of dose of calcium hydroxide – $\text{Ca}(\text{OH})_2$, or eventually of sodium aluminate – NaAlO_2 necessary for quantitative precipitation of various concentrations of sulphates is represented in Figures 1, 2 and 3. Rate of mixing of reagents should be the highest possible (process of precipitating of sulphates is controlled by diffusion of reacting ions), reaction times oscillate within range of 15-30 min.

In case of chemical precipitating of sulphates the ettringite phase has a form of cryptocrystalline (or eventually amorphous) fine-dispersed precipitate which will acquire a crystalline structure only after repeated drying and re-hydration as it was laboratorily demonstrated /5/.

Technological procedure of mine water desulphation

The newly developed technology of desulphation was verified by modelling and practical operation with sufficient evidence and high efficiency of reduction of sulphates safeguarding with big reserve below-limit concentrations of residual sulphate content for all kinds of mine water mentioned introducingly (9):

Technological procedure consists of the following three particular stages /10,11/:

1. primary alkalinizing of mine water to $\text{pH}=11-12.4$ (according to form of Al-ions dosing) by calcium hydroxide - $\text{Ca}(\text{OH})_2$ and separating of alkalification sludge by sedimenting and filtering,
2. chemical precipitating of sulphates by aluminium salts (containing either AlO_2^- or Al^{3+} ions) and separating of produced desulphation sludge by sedimenting (including flocculating) and pressure filtration,
3. neutralizing of desulphated water by means of liquid carbon dioxide – CO_2 and separating of produced neutralization sludge by sedimenting and pressure filtration.

This technology after operational verification and having fulfilled all requirements was incorporated into project documentation for complementing of existing technologies of mine water cleaning /6,7,8/.

Apart of *mine water cleanup* the technology must equally solve the problematics of sludges produced by chemical precipitation of all contaminants. It is necessary to consider all partial sludge fractions which are produced by IEI-HGF desulphation technology, i.e.:

- alkalification sludge (containing besides $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ equally the liquid phase of $\text{Ca}(\text{OH})_2$ and hydroxides of other metals),

- ❑ desulphation sludge (containing mostly solid ettringitic component and hydrated calcium aluminates),
- ❑ neutralization sludge (containing mostly carbonates and calcium hydrogencarbonates).

Alkalinification or neutralization sludges are predominantly medium dispersed and fast sedimenting even without adding flocculating agents. Desulphation sludge, fresh precipitated, is fine-dispersed and viscous, sedimenting with great difficulty. Sedimentation rate can be approximately twice increased by adding a flocculating agent. However, mixed „water treatment,“ sludge can be very well dehydrated by pressure filtration by means of filter press. Although the filtration cake still contains 70-80 per cent water (partly internal bonded), its consistence is non-adhesive and the product is well-transportable by conventional transport means /6/.

Manipulation of water treatment sludge produced by technology of mine water desulphation is as yet subject of research the aim of which is a qualified appreciation of variants concerning either disposal of the sludge or depositing of solidified sludge on open-air heap or underground, or eventually of variants requiring preliminary technological research and development aimed at finding possibilities of application of sludges of given type for recipes of production of filling and opening materials applied in fly-ash cements, cinder or slag cements, of fillings for mortars (calcined gypsum), plaster or coating materials etc.

Conclusion

Results of relatively extensive research of technological processes of desulphation of mine water from mining of coal or gypsum performed both at designer workplace of Mining Geological Faculty of VŠB – Technical University of Ostrava and in situ in modelling and pilot scale enabled development of *new method of chemical precipitation of sulphates* by combination of Ca^{2+} , OH^- ions and of ions of selected alumina (aluminate) salts. The desulphation method is ecologically as well as economically acceptable, its application is adequate not only for mine water from mining of coal, gypsum and sulphidic ores, but also for cleaning of a number of industrial waste water types with above-limit content of sulphates (for instance waste water from pickling of steel parts, from electroplating of sheets etc.). This method is sufficiently efficient as it safeguards reliably a *below-limit sulphate content*, i.e. residual sulphate content values below 300 mg.l^{-1} , but also a below-limit level of a *number of heavy metal cations* and it does not increase total salinity of cleaned-up water.

Disposal or eventual further use of produced water treatment sludges is subject of interrelated research, which is being conceived by designer workplace.

References

- [1] Píša, V.: Možnosti desulfatace důlních vod SHR (Possibilities of defulphation of mine waters in SHR). *Výzkumná zpráva VÚHU, k.ú.o., Most, 1984, 82 s.*
- [2] Volšický, Z.: Úprava obsahu síry a popelovin v hnědých uhlích SHR (Benefication of sulphur and ash contents in brown coals of SHR). *Doktorská disertace, Ostrava, VŠB, 1986, 223 s.*
- [3] Postgate, J., R.: The sulfate-reducing bacteria: Contemporary perspectives. New York - Berlin – Heidelberg, *Springer Verlag, 1992, 156 s.*
- [4] Vidlář, J. : Vývoj desulfatačních činidel pro důlní vody hnědouhelných lomů (Development of desulphation reagents for mine waters of brown-coal open-pits). - In *Sb. věd. konf. „New Trends in Mineral Processing II“*, VŠB - Technická universita Ostrava, 1997, 180-189 s.
- [5] Vidlář, J. - Fečko, P. - Schejbalová M. et al. : Studium chemických rovnováh a možností separace železa a síranů z důlních vod hnědouhelných lomů (Study of chemical equilibria and possibilities of separation of iron and sulphates from mine waters of brown-coal open-pits). - *Závěrečná zpráva projektu GAČR č. 105/96/0752, HGF VŠB-TU Ostrava, 1999, 75 s.*
- [6] Vidlář, J. - Schejbal, C. - Schejbalová, J. - Klika, Z. : Návrh technologického řešení odstraňování síranů a RL z důlních vod lokality Kateřina - Radvanice, VUD. (Project of technological solving

of removal of sulphates and dissolved substances from mine waters of Kateřina locality - Radvanice, VUD). - *Výzkumná zpráva HS 580427, HGF VŠB - TU Ostrava, 1998, 32 s.*

- [7] Malkovský, M. et al.: Geologie severočeské hnědouhelné pánve a jejího okolí. (Geology of North Bohemia brown-coal basin and vicinity). - *Academia, Praha, 1985, 424 s.*
- [8] Dopita, M. - Havlena, V. - Pešek, J. : Ložiska fosilních paliv. (Deposits of fossil fuels). - *SNTL, Praha, 1985, 263 s.*
- [9] ---: Způsob čištění důlních vod s nadlimitními obsahy síranů. (Method of cleaning of mine waters with overlimit content of sulphates). - *Patentová přihláška ČR, PV 666/97*
- [10] ---: Způsob úpravy důlních vod polyaluminiumchloridem. (Method of processing of mine waters with the aid of polyaluminiumchloride). - *Patentová přihláška ČR, PV 4786/99*
- [11] ---: Způsob úpravy důlních vod hlinitanem sodným. (Method of processing of mine waters with the aid of sodiumaluminate). - *Patentová přihláška ČR, PV 4787/99*

Resumé

Důlní vody z lomů nebo dolů, těžících hnědé uhlí, obsahují ionty síranů – SO_4^{2-} v důsledku biochemické oxidace přítomných disulfidů železa (pyrit, markazit) a vysoké rozpustnosti vzniklých oxidačních produktů. Důlní vody z těžby sádrovce (resp. anhydritu) obsahují ionty síranů v koncentracích, odpovídajících součinu rozpustnosti síranu vápenatého.

Obsahy síranů v uvedených důlních vodách vesměs vysoce převyšují přípustné ukazatele znečištění povrchových vod dle platných legislativních limitů, především dle Nařízení vlády č. 82/99 Sb., v němž je limitní ukazatel koncentrace síranů stanoven na $300 \text{ mg} \cdot \text{dm}^{-3}$.

V referátu je na podkladě diskuse o hydrogeologických a hydrochemických charakteristikách předmětných důlních vod vyznačen originální způsob desulfatace těchto vod, vyvinutý na řešitelském pracovišti – IEI HGF, VŠB-Technické univerzity Ostrava.

Jde o chemické srážení síranových iontů kombinací iontů vápníku a hliníku v silně alkalické oblasti, a to až na hluboce podlimitní zbytkové koncentrace. Desulfatovaná voda je neutralizována kapalným oxidem uhličitým.

Desulfatační kal je možno využít v silikátových technologiích nebo likvidovat ekologicky přijatelným způsobem. Postup byl verifikován v provozním měřítku.

Recenzent: Prof. Ing. Michal Leško, CSc., FBERG, TU Košice

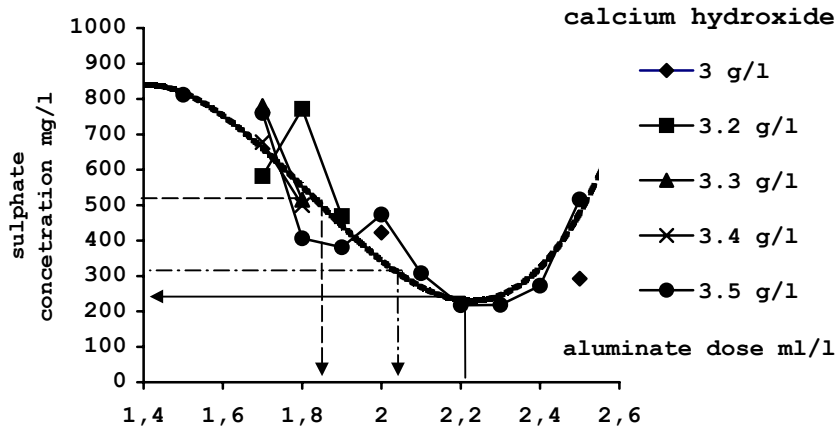


Figure 1 – Optimisation of reagent regime of desulphation in laboratory of ČDV Kateřina-Radvanice. Samples 5 l, 500 rpm. Dose – 30 % NaAlO₂

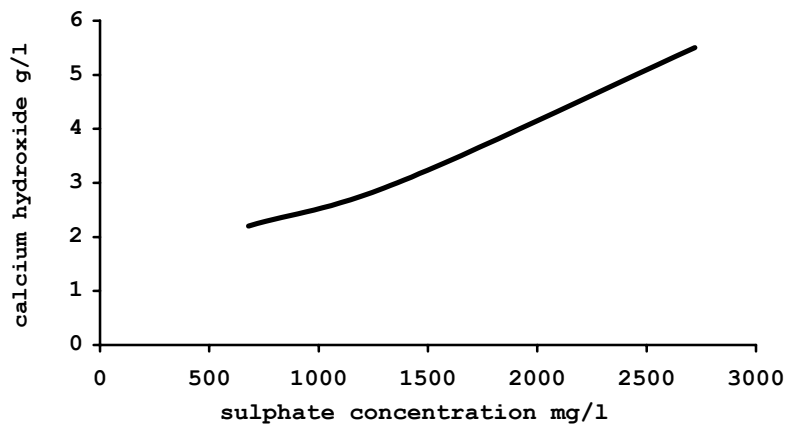


Figure 2 – Diagram of dependence of calcium hydroxide on concentration of sulphates

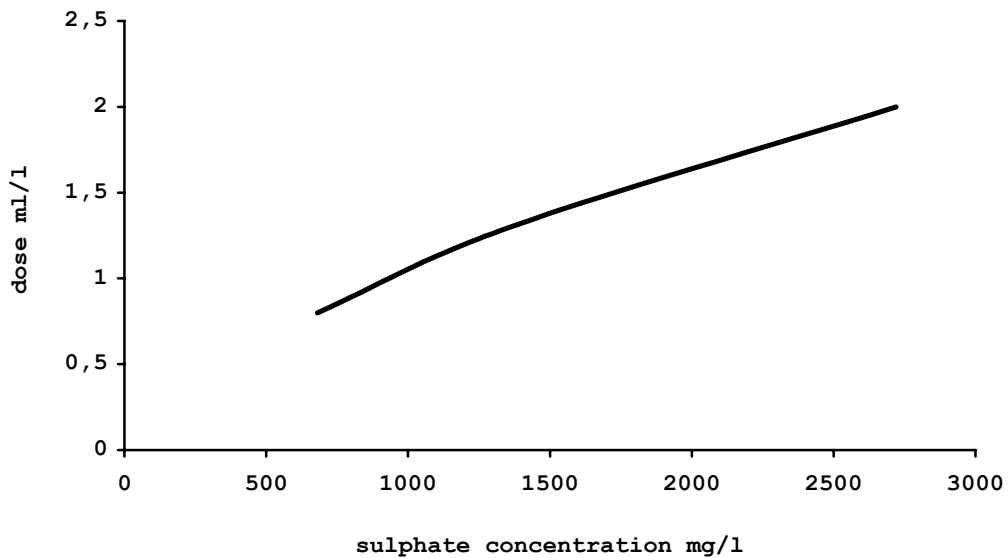


Figure 3 - Diagram of dependence of aluminate dose on concentration of sulphates
Dose – 30 % NaAlO₂