UTILIZATION OF SALT MINE WATERS IN THE MEANS OF ENVIRONMENTAL PROTECTION

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ABSTRACT

One of the river pollution sources are saline mine waters ejected from the Upper Silesian coal mines. Salinity of some effluences exceeds 200 g/dm^3. An intensive development of coal mining increases the amount of water and salt disposed into the rivers. It has been found that the greatest salinity is affected by the mines ejecting waters containing over 70 g/dm^3 NaCl. Such big contents of sodium chloride in the total amount of disolved salts caused that the investigations concerning salt mine waters utilization have been undertaken. The result of these investigations is protection of water against salination. The Central Mining Institute has developed a new technology of producing the sodium chloride and potable water from saline waters obtained from mine drainage without chemical pretreatment of brine. On the basis of this technology, in Dębieńsko mine the pilot plant operating on industrial scale has been put into operation in 1975. The plant output is 100 m^3/h of brine. The operation data of this plant has been discussed in this paper. As a result of operation of this plant, various usable products are obtained: table salt, desalinated water and wastesgypsum and mother liquor.Solid wastes do not cause any problems in their utilization. However, mother liquor storage causes the danger of secondary water pollution. Considering above, the conception of wasteless utilization of all components contained in the mother liquor has been presented. The wasteless utilization of saline mine waters allows to protect effectively the environment as well as to obtain useful products.

INTRODUCTION

Deterioration of superficial waters quality is a very serious problem in the Upper Silesian water economics. This problem arised due to dynamic development of industry and mining in this area. Coal mining contributes greatly in water pollution with mineral salts. The deep-level underground mining is accompanied with natural water effluences from excavations that are pumped out onto the surface.

A degree of mine water salinity varies, from water of drinking water quality to brines of sodium chloride concentration up ot 200 kg/m³.

Fresh waters occuring in mines suitable to have a separate water intake, are utlilized by the mine itself or directed to the municipal water pipe network or to the neighbouring industrial plants.

Saline mine waters disposed into the rivers cause a greater salination of the latter. It limits usability of river waters for population demands, agriculture as well as industrial purposes. The cost of superficial treatment increase at the same time.

The localization of the Upper Silesian Coal Field almost at the springs of Vistula and Odra rivers causes their absorbing capacity of salts to be small due to a low water flow in these rivers. At the same time, the industry concentrated in an upper part of Vistula and Odra rivers basin consumer large quantities of industrial water and produces a considerable amount of liquid wastes.

The increase of coal production is performed by shafting in new mines and development of the already existing ones, mainly by their deepening. It causes an increase of natural mine effluents and of salt concentration in these waters. Simultaneously, industry development in the Upper Silesian Industry Region increases demands for potable water. All of it makes the situation of water economics difficult in the Region. On the one hand, pollution of potable water increases, on the other hand one demands for it increase.

Characteristics of mine waters are given in another paper /1/.

CONCEPTION OF LIMITING THE SALINATION OF SUPERFICIAL WATERS WITH SALINE MINE WATERS

Protection of river waters against their salination with saline mine waters is a very difficult problem for coal mine water management. The only effective way of superficial water protection against salination would be to

stop disposal of saline mine waters into the rivers. This solution is technically impossible under current conditions, because of large quantity of saline mine waters having different salination. Utilization of such quantity of brines would require a significant quantity of energy and other materials. At the moment our economy manage with this problem.

Selecting in mine the waters of different salination enables separate pumping out the mine brines of concentration exceeding 70 kg/dm^3. These brines may be a raw material for chemical industry.

Investigations carried out by the Department of Mining since many years resulted in two methods of decreasing the excesive salination of rivers: hydrotechnical method for saline waters of concentration below 70 kg/m^3, and utilization for mine brines concentration exceeding 70 kg/m^3 /2/.

In general the hydrotechnical method consists in accumulation of saline mine waters in large reservoirs and controlled drainage of the waters into the river at acceptable concentration of salt in water for the particular class of river purity.

The utilization method consists in production of table salt and fresh water from mine brines or in such a processing of brine that it becomes a raw material for chemical industry.

Complex river protection due to quantities of mine waters and different degree of their salination requires the combined treatment methods to be used.

The use of typical salt evaporation method in case of utilization method would require softening of mine brines. In this case, cost of chemicals used for pretreatment could reach 60 per cent of actual salt price due to brine hardness. For this reason, a method of NaCl and $CaSO_4$ crystallization without their previous softening using chemicals has been developed /3/.

The whole process of initial brine preparation consists in sedimentation, filtration, carbinate decomposition and degassing.

Calcium is removed during process as a calcium sulphate, while magnessium and other pollutants are removed as mother liquor. Calcium can be removed during reversed vaporization owing to the properties of $CaSO_4$ such as: solubility, ability to form a supersturated solution having a long period of metastability, ability to form compact slurry and fine thin suspension /4/.

DESCRIPTION AND OPERATION OF PLANT DESIGNED FOR MINE WATERS UTILIZATION

The flow-sheet of plant for mine water desalination is

presented in Fig.1. The key point of this technology consists in that the initial purification of brine prior to thermal concentration covers only the removing of solids suspension, decarbonization with sulphric acid, stochiometric adjustment of Ca^{2+} and SO_4^{2-} ions, thermal degassing and alkalization. The initially treated feed brine is supplied to a circulating brine just before the regenerative heat exchangers. The mixture of circulating brine and initially prepared feed brine is heated up to a temperature of 100 °C inside the regenerative heat exchangers which are simultaneously used as condensers of vapours from brine concentrating process. The brine is then heated up to a temperature 120°C with saturated steam in heat exchangers. When the brine is heated up, crystallization of calcium sulphate proceeds in high volume crystallizers of special design. Then, brine is supplied to a series of 12 flush chambers, where it undergoes concentration through water vaporization. Most of this water (from the first stage of evaporating) is recovered as a desalinated water. The last stage vapours are condensated in jet condensers and they are used to refill cooling water circulation system. Sodium chloride crystallizes from the concentrated brine in the last stages of flash chambers and is separated in the salt separator. The purity of obtained salt depends on the composition of circulating brine. In the process, some difficulties were encountered concerning both crystallization and removing the calcium sulphate from the plant.

Under operating conditions, it appeared that when thermodynamical parameters and rate of circulating brine were not satisfied, scaling of heat exchanger pipes or formation of very fine $CaSO_4$ slurry which did not remain in gypsum crystallizer have occured. The crystallization of $CaSO_4$ is a very sensitive process and requires to follow all thermodynamical parameters of the process /5/.

Operating experience shows, however, that it is possible to protect heat exchangers scaling and $CaSO_4$ precipitation in crystallizers in a form of loose suspension of crystallites about 20 µm dia. Hitherto industrial experiments have shown that it is possible to eliminate circulating filtration as foreseen previously from pilot scale results/4/.

Table salt obtained in the separator is subject to a standard treatment, i.e. centrifugation and thermal drying. Basing on this technology /PRL patent, N° 50342/, the pilot industrial plant of capacity of 2400 m^3 mine brine daily (salt concentration being 100 kg/m^3) was put into operation in 1975. This plant operated continuously, producing desalinated water and salt (purity of over 99.6 %) the latter of commercial value. The desalinated water of salts concentration below 100 mg/dm^3 TDS is treated in ion-exchanger in order to remove ammonia ions and then supplied to mine as a potable water /6/.

On the basis of industrial experience typical desalination industrial plant has been designed (capacity of 2400 m^3/day of brine). They will be erected at coal mines. The plants operating according to the technology discussed above can be also used in other plants where the highly saline waters are to be processed.

Apart from basic products such as table salt and desalinated water are also formed waste products /7/: separated in preliminary brine purification,
- calcium sulphate precipitated during evaporating process,
- mother liquor containing considerable quantity of magnessium chloride apart from potassium, iodine and bromide chlorides.

This mother liquor is 1-4 % of utilized brine depending on brine composition and concentration rate. The solid wastes do not cause any problems because they can be stored together with other mine wastes.

But storage of mother liquor within the mine area creates a danger of secondary water pollution. Thus the conception of complex utilization of all components contained in the mother liquor has been presented.

The mother liquor of this type may be used as:
- antifreezing agent for turnouts, not loose materials, sprayers for roads during winter season, etc. in the form of concentrated aolution,
- raw material for sodium and potassium chlorides and magnessium salts.

Magnessium salts can be processed further to obtain magnessium oxide that is a desirable raw material for manufacturing the refractor materials. The mother liquor utilization as a antifreezing agent does not make any technical problems and is out of comment. The mother liquor processing is complicated and requires additional energy consumption.

MOTHER LIQUOR PROCESSING

The basic component of mother liquor is magnessium chloride and the whole utilization technology consists in its separation. Two methods were used during utilization tests:
- separation of NaCl, KCl, iodides and bromides to obtain pure solution of $MgCl_2$,
- reaction of $MgCl_2$ to insoluble compounds and their separation.

In the first method high energy consumption is required and a loss of magnessium occurs due to double salt formation, that results in solutions with residual NaCl and KCl contents.

The second method, depending on selection of reagent enables to recover magnessium almost entirely, however, some wastes are formed, the utilization of which is rather troublesome.

Basing on the laboratory data the method of wasteless mother liquor utilization has been developed the flow-sheet of which is presented in Fig.2. In this plant, of nominal capacity of 4 m^3/h, its to be to utilize the whole mother liquor from the pilot desalination plant /8/.

The technology designed comprises:
- in the first stage - deiodination and debromination by the known method comprising J_2 and Br_2 desorbtion with air from acidified mother liquor and successive its absorption from basic liquor,
- in the second stage - thermal conventration of mother liquor accomplied with crystallization of salt returned to desalination installation due to its low purity,
- in the third stage - crystallization of artificial carnalite from a concentrated liquor followed by potassium chloride separation,
- in the fourth stage - concentration of the remaining liquor and magnessium chloride separation.

This plant will be tested in terms of selecting the optimum mother liquor utilization technique suitable on industrial scale after a previous separation of iodine and bromine. In iodine and bromine recovery section, an important problem will be testing and selection of constructional materials for equipment exposed to an especially intensive corrosion.

OTHER SOLUTIONS

In search of other methods allowing to restrict brine disposal to superficial waters, the possibilities of direct mine brine utilization in chemical plants, where table salt is used as a raw material are currently investigated. At present basing on the technology developed by the Institute of Chemical Technology, Silesian Polytechnical University Gliwice, the pilot plant for chlorine manufacture from mine brines is under construction /9/.

The technology of chlorine manufacture from mine brines comprises:
- precipitation of Mg^{2+} ions with soda lye obtained from the saline lye concentration process: magnessium hydroxide sludge obtained can be used for further processing while filtration is recirculated,
- brine concentration up to a concentration of NaCl of 160 g/dm^3,
- precipitation of Ca^{2+} ions using a soda - lye method and small amount of Mg^{2+} ions unprecipitated in the first stage (soda lye is from basic liquor concentration process),
- resaturation of brine with salt precipitated in brine-lye concentration, filtration and pH adjustment using hydrochloric acid,

- electrolysis of resaturated brine to obtain chlorine, hydrogen and basic liquor,
- concentration of basic liquor to obtain salt and sodium hydroxide.

In this year. it is planned to put the plant into operation and perform investigation works the aim of which is to test the performance of the technology developed. The method of concentration of moderately salinated mine waters using membrane techniques have been also investigated /10/.

These methods used in the first desalination stage would allow to obtain potable water, being in deficite in the Upper Silesian Coal Region. Application of these methods according to the authors' opinion, depends on know-how production of durable and cheep ion-exchange membranes in Poland, decrease of energy consumption and preparation of brines of salt conventration about 100 g/dm^3. These brines could be processed further to salt and water using a vaporization method.

These solutions shall be considered only for future use and attainable only in respect of fresh water shortage coverage, when other fresh water sources will be depleted. The general concepts of solving the water protection against salination by mine waters are very difficult to be attained from both technical and economical viewpoint. Optimalization of the solution requires to be considered in respect of total economics and co-operation of many departments.

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LIST OF FIGURES:

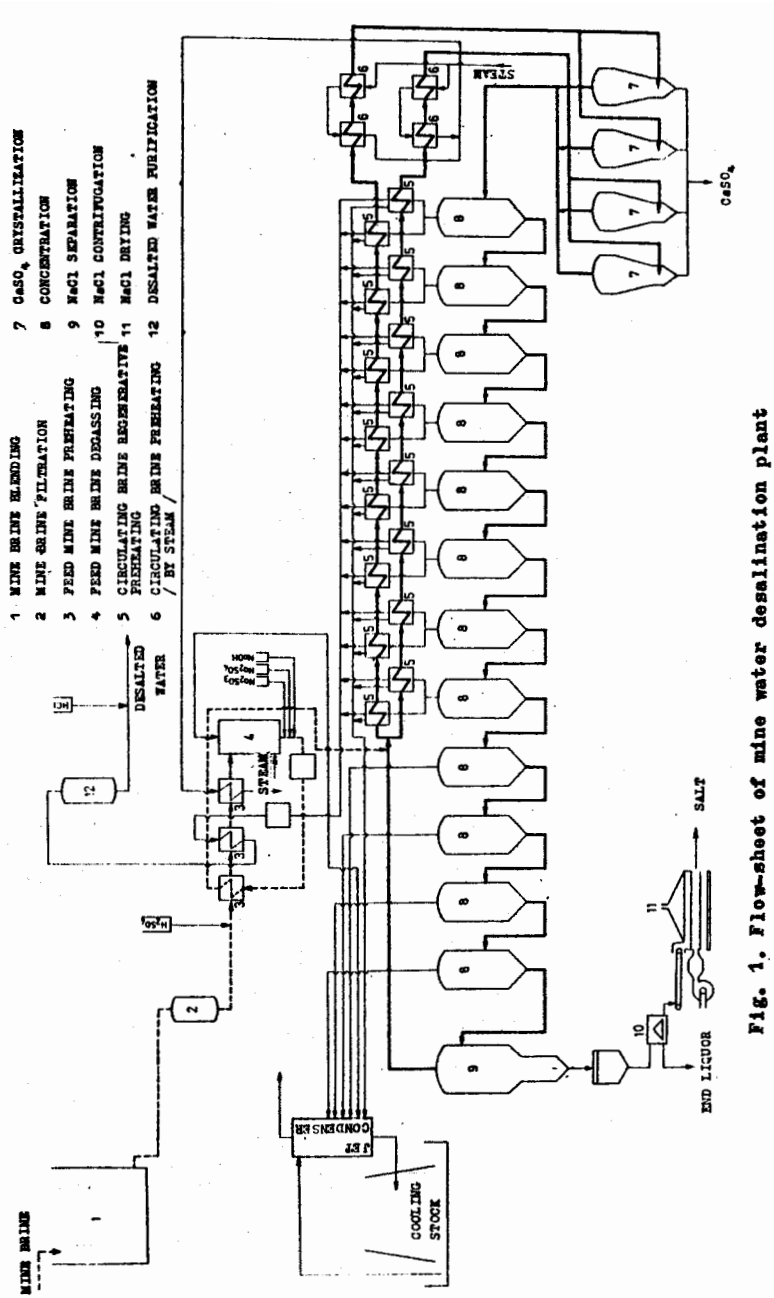

Fig. 1. Flow-sheet of mine water desalination plant

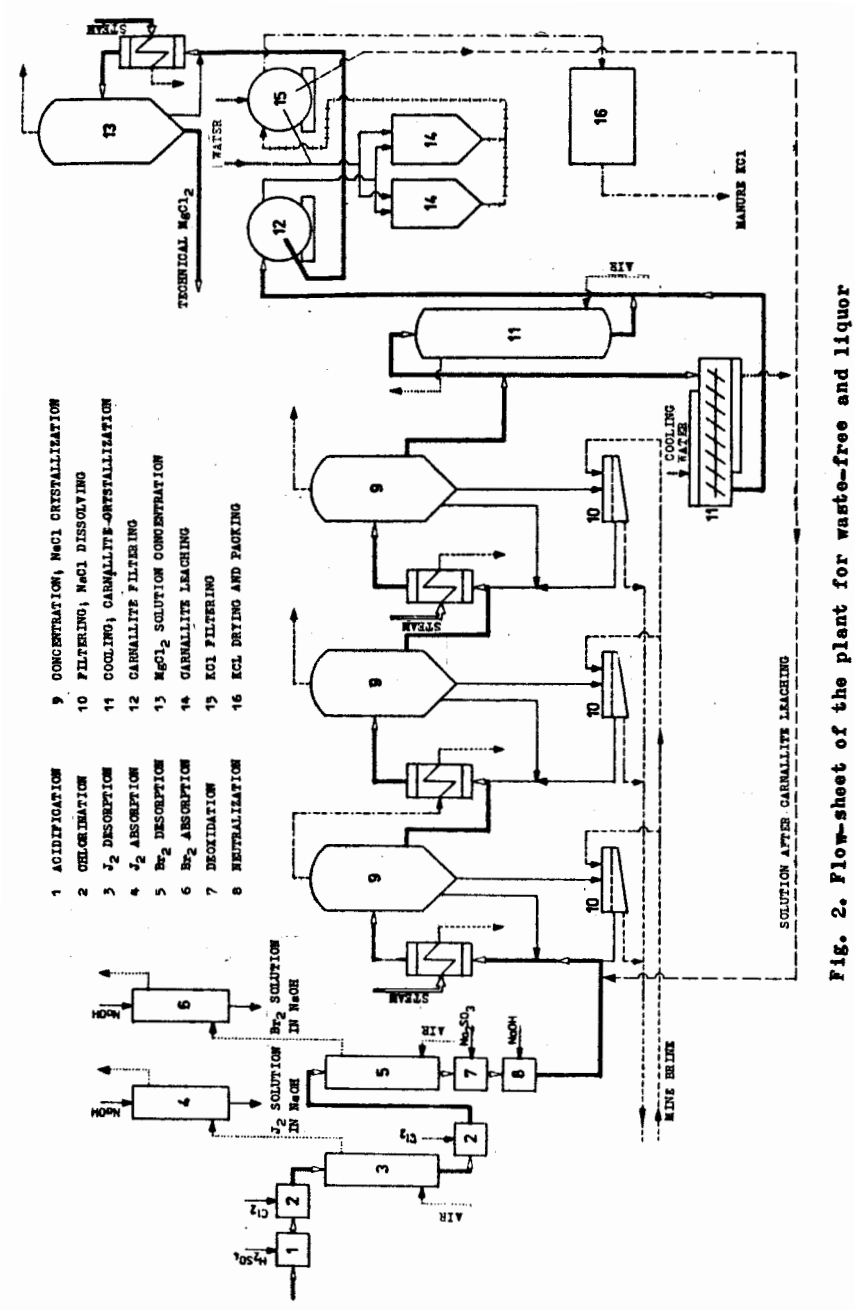

Fig. 2. Flow-sheet of the plant for waste-free and liquor