*Desalination and Water Treatment*
www.deswater.com

33 (2011) 36–43
September

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doi: 10.5004/dwt.2011.2616

# Treatment of ammonia-polluted groundwater in North Bohemian brown coal mining region — Feasibility study

M. Kubal, M. Podhola, T. Patočka, K. Ciahotný, M. Kuraš*

*Institute of Chemical Technology, Faculty of Environmental Technology, Technická 5, Praha 6, 166 28, Czech Republic*
*Tel. +420 (2) 2044 4114; Fax +420 (2) 2044 5029; email: Mecislav.Kuras@vscht.cz*

Received 20 January 2010; Accepted in revised form 6 October 2010

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## ABSTRACT

A feasibility study was completed to assess the applicability of reverse osmosis technology at the site, where a brown coal processing plant released 4000 ton of ammonia into the subsurface during 20 years. The present groundwater ammonia concentration (approx. 100 ppm) was required to be reduced to 0.5 ppm to satisfy the Czech groundwater remediation directives. The reverse osmosis principle was examined within this study with the aim to confirm its capacity to reach the ammonia remediation limit as well as to provide cost estimation. The technological process was simulated by means of pilot-scale installation using samples of contaminated groundwater. Reverse osmosis clearly demonstrated its capacity to clean up the ammonia polluted groundwater to the limit demanded.

*Keywords*: Polluted groundwater; Ammonia; Remediation; Reverse osmosis

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## 1. Introduction

The North Bohemian region of the Czech Republic can be characterized by extensive exploitation of the local brown coal resources, which in the recent history were also providing raw materials to the production of synthetic fuels. The technologies for brown coal conversion to synthetic fuels by high pressure hydrogenation of brown coal tar with sulphide catalysts (Bergius process) were installed at the plant situated between the cities Most and Litvinov (approximately 80 km north-west of Prague). The plant was founded — in at that time occupied territory — by Nazi Germany as the Sudetenlandische Treibstoffwerke AG in October 1939, a part of Hermann Göring Werke, to produce liquid fuel, which was a critical item for military forces. Later, past 1945, the plant was renamed to Joseph Stalin Chemical Enterprises, where synthetic fuels production was running until 1975. Today the area is owned by Chemopetrol a.s. company.

There were two main waste products released from the coal processing — ash and tar. The ash was progressively accumulated over an area of about 0.4 km$^2$ during the whole period of operation of the coal–liquid fuel conversion process (1943–1975). This area was called as “ash depository”. Besides ash and tar, the plant produced large volumes of ammonia containing wastewater, which could not be treated before release since the factory was not equipped with a wastewater treatment facility during this time period. Based on the assumption that the ash depository could provide some sorption capacity, the ammonia containing wastewater was rejected directly into this area. A certain amount of ammonia was adsorbed onto the ash particles, while the remaining part penetrated into the groundwater. The wastewater discharge into the ash depository was stopped after a treatment unit was installed in the plant.

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* Corresponding author.

*Presented at the 2nd International Conference on Environmental Management, Engineering, Planning and Economics (CEMEPE), Mykonos, Greece, June 21–26, 2009.*

Systematic monitoring of the pollution concentrated at the area around the former synthetic fuels processing plant (carried out in 1996–1997) showed that the ash depository was heavily contaminated with about 4000 ton of ammonia. To limit ammonia emission to the atmosphere as well as rainwater penetration into the ash depository body its surface was covered with low permeable clay layer during the years 1999–2002. In this way, however, the ammonia oxidation processes were restricted since air penetration rate through the clay is very slow. Currently the main risk associated with the ash depository ammonia is potential contamination of a new Lake Most, forming now by flooding of a former brown coal strip mine situated in close proximity to the ash depository and having an area of more than 3 km$^2$ (Fig. 1). The northern part of the lake will be practically in contact with the ash depository. Since the current groundwater flow in this area is directed from the depository towards the lake, it was requested by Ministry of the Environment of the Czech Republic to identify and demonstrate an effective and economically acceptable process to remove ammonia from the groundwater flowing into the lake. Preferred by the ministry was the on-site treatment installation which would protect the lake from ammonia penetration and which further would, if possible, process the ammonia to the form of fertilizer applicable to recultivation of the brown coal mining area.

Hydrogeological modeling of the area around the plant suggested that the total amount of contaminated groundwater flowing from the ash depository into the Lake Most would be approximately 12,000 m$^3$ per month, while the actual average ammonia concentration was estimated to be about 100 ppm with possible fluctuation within the range from about 50 to 300 ppm. No other pollutants were expected to be present in the groundwater in significant amounts. Systematic groundwater monitoring further showed that the dominant form of ammonia was ammonium bicarbonate, with a pH value of 8.6. The concentrations of other ions in the solution ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $SO_4^{2-}$) were insignificant. Thus the goal of this study was to demonstrate a suitable technological process having the capacity to reduce the ammonia concentration in the groundwater from the initial concentration of approximately 100 ppm to the limiting value, which was considered in two variants — 3.0 ppm and 0.5 ppm, where the latter was in agreement with current directives.

Air stripping and reverse osmosis principles were selected first within this feasibility study as the two water treatment processes potentially suitable for cleaning up the contaminated groundwater with an ammonia concentration of approximately 100 ppm, as was found in the ash depository.

Ammonia air stripping from wastewater streams is generally considered to be an efficient process for the input concentrations of about 100 ppm under assumption that well-established constructions are installed (counter-

Fig. 1. View towards the area of the future Lake Most (right centre), the former synthetic fuel plant is situated in the upper left position and the ammonia contaminated ash depository is circled by the white line.

current or cross-flow stripping towers) and suitable operational conditions (pH value, temperature) are ensured [1]. General suitability of the air stripping principle was further supported by its frequent industrial applications for ammonia containing streams, for example in case of wastewater from gasworks and cookeries [2] or sugar industry [3]. Relevant references can also be identified for the laboratory and pilot-scale studies directed to chemical engineering aspects of ammonia stripping [4–6], or to its specific applications in agriculture or food industry [7–10] or for treatment of contaminated groundwater and depository leachates [11,12]. More detailed investigation within the above references identified, however, a significant technical drawback of the ammonia stripping process consisting in very low ability of ammonia to be transported from the aqueous solution to the air at ambient temperatures. This fact would most probably result in unacceptably complicated technical solution, so ammonia stripping was not considered for further experimental examination.

The membrane treatment potential for ammonia removal mainly followed from the general capacity of reverse osmosis process to separate monovalent ions from the aqueous solutions. Recently the ammonia removal from wastewater through reverse osmosis installations was studied in connection to mining and coke industry demands [13,14,22], agriculture production [15,16], depository leachates [17,18, 21] and surface water or wastewater [19,20, 23].

Regardless the items listed above, no reference was identified dealing with the reverse osmosis plant operated under the conditions and requirements similar to those described in this work. Thus the general goal of this study was to assess the technical and economical acceptability of the reverse osmosis process to treat the ammonia polluted groundwater at the Lake Most area. The particular goals of the work included: 1) defining functionality of the reverse osmosis unit for the ammonia containing aqueous solution using different operational pressures, temperatures, pH values and ammonia input concentrations, 2) showing the influence of the ammonia counterions to process performance, 3) designing the reverse osmosis technological scheme (with final ammonia concentrates expected in the form of fertilizers) and estimating the capital and operational costs.

## 2. Materials and methods

The reverse osmosis process was simulated by using a pilot scale LAB-M20 unit (Fig. 2) supplied by Memsep Co., Prague, Czech Republic, which basically consisted of a 30 L accumulation tank (B), a high pressure pump (C), an universal membrane holder for ultrafiltration, nanofiltration and reverse osmosis membranes (H), and a heat exchange unit (D). A stack of 20 flat reverse osmosis membranes with a total area of 0.5 m$^2$ was used for the groundwater treatment simulations. The membranes HR-98 PP (regenerated cellulose on polypropylen) were supplied by Alfa Laval (Alfa Laval Corporate AB, Lund, Sweden). The LAB-M20 pilot scale unit equiped with HR-98 PP membranes was generally able to simulate reverse osmosis separation process within an operational pressure range between 0–5 MPa, a temperature range between 10–30°C, and a pH range between 2–10. The choice of the membranes for pilot scale examination was supported by references provided by the LAB-M20 unit supplier, which recommended the HR-98 PP type for its high operational reliability.

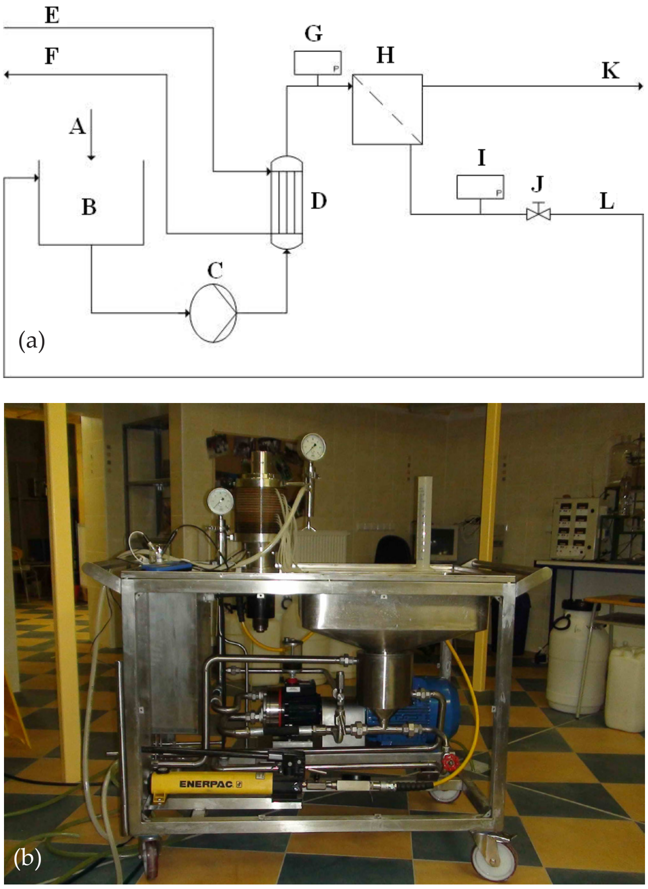

Fig. 2. Reverse osmosis pilot scale unit LAB-M20: (a) schematic representation, (b) total view.

The reverse osmosis LAB-M20 unit was operated in batch mode using a 30 L feed of ammonia polluted groundwater in each run, which was processed to the predefined volumes of permeate and concentrate. Thus, two final samples resulted from each reverse osmosis simulation — the permeate and the concentrate — which were analyzed for ammonia concentration using UV-VIS spectrophotometry method CSN ISO 7150-1 (757451). The polluted groundwater was delivered from the locality in the amount of about 4 m$^3$ before starting the experiments. The input groundwater analysis showed the pH value

8.6 and the following contents of the major components: $NH_4^+$ = 104 ppm, Na = 86 ppm, K = 45 ppm, Ca = 68 ppm, Mg = 24 ppm, Fe = 0.47 ppm, $Cl^-$ = 104 ppm, $SO_4^{2-}$ = 88 ppm, $NO_3^-$ = 43 ppm, $PO_4^{3-}$ = 9.7 ppm. The reverse osmosis experiments were performed to examine the influence of operational pressure, temperature and feed water pH values to the membranes performance, as well as to study the effect of the counterions.

## 3. Results and discussion

The reverse osmosis operation for different pressures is presented in Fig. 3, where concentration factor $C_F$ (ratio between the total feed volume and concentrate volume) is used as an independently variable. Permeate flux per membrane unit area and rejection (difference between feed and permeate concentration related to feed concentration) are used to assess the membrane performance. It follows from Fig. 3 that the permeate flux exhibited almost linear increase with operational pressure keeping practically the same rejection values. The ammonia concentrations measured in the mixed permeate (accumulated within each run) were 26.9 ppm, 27.4 ppm, 29.1 ppm, 26.5 ppm, respectively, for the operational pressures 1–4 MPa. Thus the operational pressure had no significant influence to the quality of the permeate. The value of 2.0 MPa was then selected for the subsequent experiments — it provided satisfactory permeate flux and may easily be obtained in cheaper installation equipped with plastic pipelines.

The influence of membrane operational temperature on the permeate flux and rejection is shown in Fig. 4, where the results of the experiments carried out at the operational pressure 2.0 MPa are presented. It is obvious that the change in operational temperature caused notable difference in the permeate flux, while rejection values remained without remarkable influence. Thus the quality of the permeate showed no significant deviations within the temperatures 15–30°C, which suggested, for example, stable membrane performance through different periods of year. The ammonia concentrations measured here in the mixed permeate were 27.2 ppm, 28.6 ppm, 27.1 ppm, 27.8 ppm, respectively, for the operational temperatures 15, 20, 25, 30°C.

Further set of the reverse osmosis experiments was carried out for different pH of the feed water. Here the

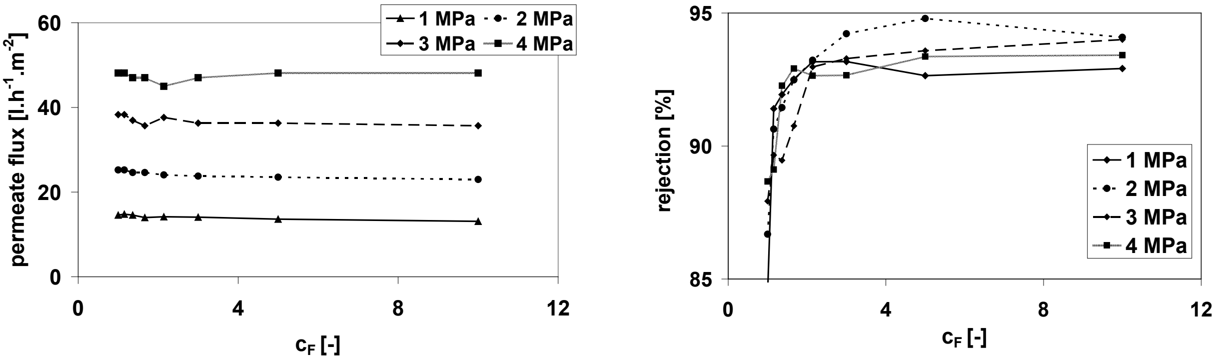

Fig. 3. The dependence between permeate flux (a), $N_{amon}$ rejection (b), respectively and concentration factor for different operational pressures (temperature 20°C).

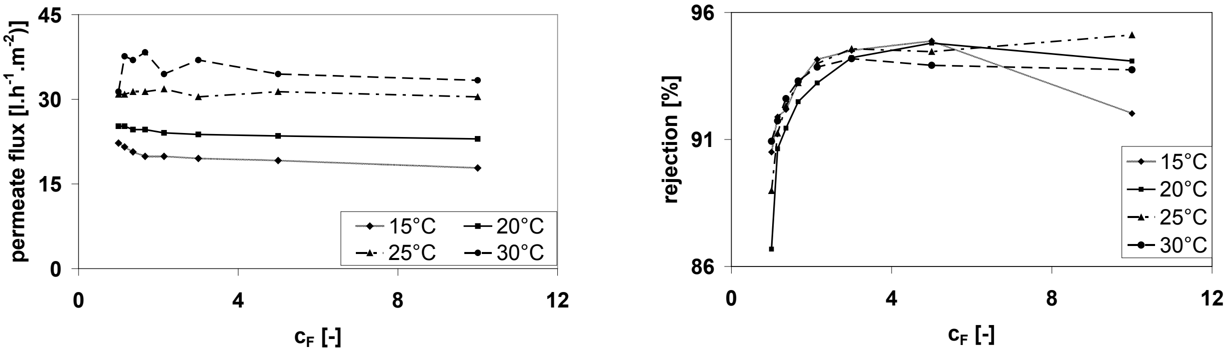

Fig. 4. The dependence between permeate flux (a), $N_{amon}$ rejection (b), respectively and concentration factor, for different operational temperatures (pressure 2.0 MPa).

pH values in the feed were set up by means of sodium hydroxide or hydrochloric acid to the values of 4.0, 7.0, 8.0, 10.0, respectively prior to introduction to the pilot scale unit. Ammonia may generally be present in the aqueous solution in ionic and nonionic forms. Ionic form $NH_4^+$ dominates under acidic conditions, while nonionic $NH_3$ form is stable under alkaline conditions. The redistribution between these two forms proceeds mainly within the pH range ~4.0–11.0, with about 50:50 ratio typically about the pH value about 9.4. The results presented in Fig. 5 show low membrane performance at pH = 10, where approximately 80% of all ammonia is present in nonionic form, which exhibited tendency to penetrate into the permeate. The ammonia concentrations measured here in the mixed permeate were 10.3 ppm, 17.1 ppm, 16.6 ppm, 72.8 ppm, respectively, for the feed pH values 4.0, 7.0, 8.0, 10.0.

The influence of starting ammonia concentration in feed water to the permeate flux and rejection is shown in Fig. 6. The starting concentrations lower than 100 ppm were reached by diluting the stock groundwater by distilled water, while higher concentrations resulted from addition of defined amounts of ammonium bicarbonate (Sigma-Aldrich). Significant decrease in permeate flux was observed for the highest feed concentration used, while the permeate quality remained practically the same for all the starting concentrations, as evidenced in Fig. 3b. The ammonia concentrations measured here in the mixed permeate were 13.8 ppm, 19.1 ppm, 25.4 ppm, 162 ppm, 308 ppm respectively for the feed concentrations 50, 75, 100, 500, 1000 ppm, respectively.

The last set of the reverse osmosis experiments was carried out for different ammonia counterions. The results shown for ammonium bicarbonate were measured using the original groundwater, while the data for ammonium sulphate, molybdenate, chloride and hydrogenphosphate were measured with artificially prepared aqueous solutions (salts from Sigma-Aldrich and Fluka). The experiments with different counterions were carried out to follow their influence to the membrane performance, mainly to the residual concentration of ammonia in permeate. Here the ammonia concentrations measured in the mixed permeate were 4.8 ppm, 5.2 ppm, 7.0 ppm, 23.4 ppm, 6.8 ppm, respectively, for sulphate, molybdenate, chloride, bicarbonate, hydrogenphosphate, respectively. Thus the presence of foreign anions could positively

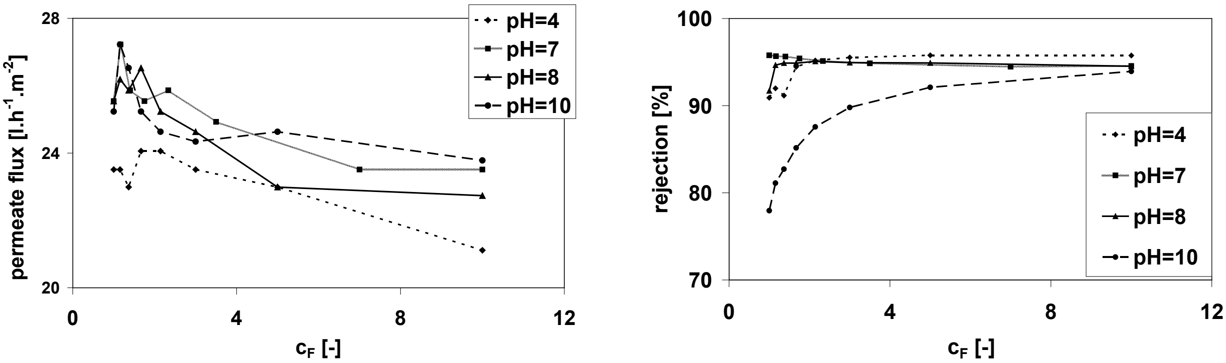

Fig. 5. The dependence between permeate flux (A), $N_{amon}$ rejection (B), respectively and concentration factor, for different feed pH values (pressure 2.0 MPa, temperature 20°C).

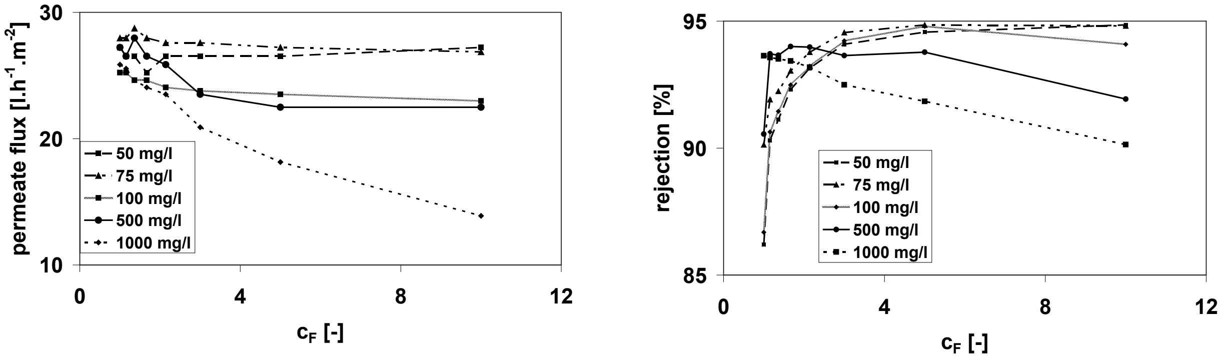

Fig. 6. The dependence between permeate flux (A), $N_{amon}$ rejection (B), respectively and concentration factor, for different feed ammonia concentrations (pressure 2.0 MPa, temperature 20°C).

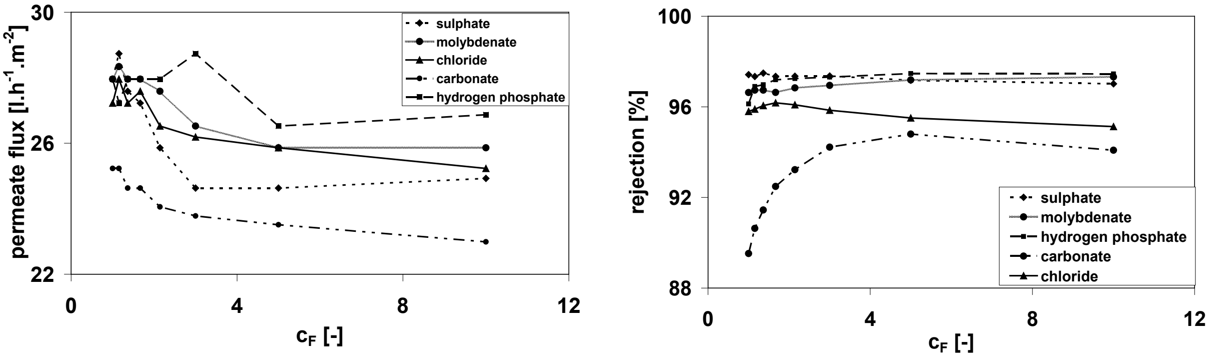

Fig. 7. The dependence between permeate flux (a), $N_{amon}$ rejection (b), respectively and concentration factor, for different foreign ions added to feed water (pressure 2.0 MPa, temperature 20°C).

influence the efficacy of the reverse osmosis treatment. The addition of foreign anions would, however, bring no principal simplification to the technological arrangement discussed further.

Based on the results of the pilot scale experimental simulations the full scale technological system was suggested, as shown in Fig. 8. The ammonia containing groundwater is driven to the accumulation tank first to balance the fluctuations in pumping rate, which is followed by the MyCelx pretreatment member responsible for removal of random trace amounts of organic compounds. Then a double stage reverse osmosis module is employed, in which permeate from the first stage (12 ppm of residual ammonia) is driven as a feed stream into the second reverse osmosis stage. The permeate from the second stage should satisfy the limiting value demanded for treated water rejection to the Lake Most (0.5 ppm), while the second stage concentrate (62 ppm ) can be returned to the beginning of this module and added to feed stream. The expected one month volume of contaminated groundwater — 12 000 m$^3$ — can, therefore, be separated in two parts: 90% consisting of treated water and 10% consisting of the first stage concentrate with ~900 ppm of ammonia. The volume of this concentrate is still too high for further processing, so an additional one stage reverse osmosis module was suggested for the full scale arrangement to reduce the 1200 m$^3$ volume of the first stage concentrate to approximately 150 m$^3$/month of final concentrate. A supplementary sorption unit filled with Clinoptylolite (natural zeolite with high affinity to ammonia) is suggested following the final permeate output to keep the ammonia residual concentration stable. The final ammonia concentrate is introduced to the precipitation unit, where most of the ammonia is transferred to the form of solid ammonium magnesium phosphate, while the remaining nonprecipitated part is returned to the third reverse osmosis stage. It follows that there would be only three products leaving the technological system designed: 1) the treated water discharged into the lake, 2) Clinoptylolite filling saturated with ammonia, and 3) precipitated ammonium magnesium phosphate. The last two products may advantageously be used as fertilizers within the recultivation works, which are continuously running at the mining region around the Lake Most. Thus the requirement demanded by Ministry of the Environment of the Czech Republic was basically satisfied through the proposal and pilot-scale demonstration of the reverse osmosis based system illustrated in Fig. 8.

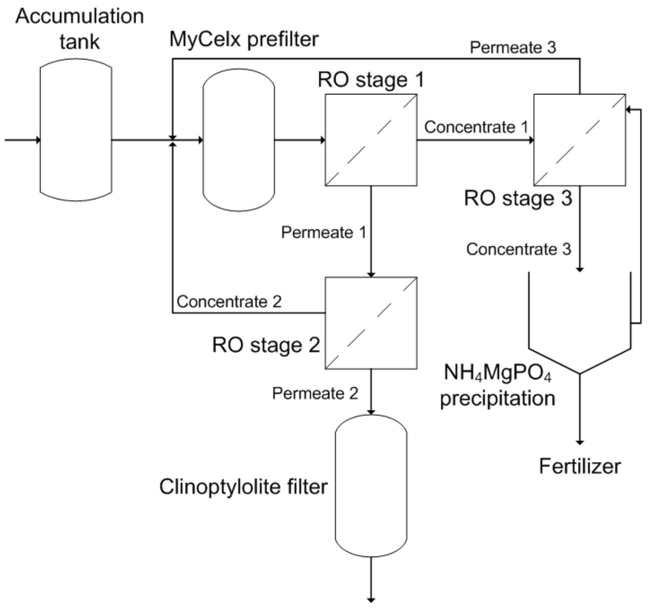

Fig. 8. Schematic representation of the full scale reverse osmosis plant suggested for treatment of the ammonia polluted groundwater.

Real applicability of the groundwater treatment system suggested in Fig. 8 would be conditioned by its economical characteristics — such as acquisition costs, operational costs, labour costs and others. The estimation of some of these costs is provided in Table 1. The data listed here are based on the consultations with private companies currently working on environmental market

Table 1
Cost estimation to the full scale treatment system illustrated in Fig. 8

| | |
|---|---|
| Capital expenditures (including pipelines, pumps and control systems necessary for each item) | – Accumulation tank (€8000)<br>– MyCelx prefilter (€6000)<br>– Reverse osmosis installation (€282,000)<br>– Clinoptylolite sorption unit (€15,000)<br>– Precipitation unit (€54,000) |
| Sub-total | €365,000 |
| Annual operational and maintenance costs | – MyCelx prefilter (€3000)<br>– Reverse osmosis modules (€9600)<br>– Clinoptylolite sorption unit (€2000)<br>– Precipitation unit (€7700) |
| Sub-total | €22,300 |
| Annual labour costs | Supervision approx. 2–3 h a day (€18,000) |
| Sub-total | €18,000 |

of the Czech Republic. It is obvious that the cost estimation provided in Table 1 has only limited reliability, since no realistic information was available for example to the administration expenses, indirect costs, taxes, or companies profit. Irrespective of this the data completed in Table 1 show relatively low level of capital, operational and labour costs suggesting that the final unit price for treatment of ammonia contaminated groundwater could move within quite reasonable range.

## 4. Conclusion

The reverse osmosis process was examined within a feasibility study completed for a site heavily contaminated with ammonia. The goal of the study was to design a treatment facility, which could reduce the ammonia concentration in groundwater from its original concentration of about 100 ppm to the limiting residual value 0.5 ppm. The results completed by means of a pilot scale reverse osmosis unit confirmed the practical applicability of this membrane separation principle for the contaminated site considered. Double stage reverse osmosis system was suggested to lower the groundwater ammonia content to the limiting value, with one additional membrane unit for further thickening of the concentrate from the first stage. The total capital expenditures for the technological system suggested were estimated about €365,000, with annual operational and labour costs of about €40,300.

## Acknowledgment

This work was completed within a research plan MSM 6046137308 supported by Czech Ministry of Education, Youth and Sports.

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