

# TREATMENT OF BRINES USING COMMERCIAL ZEOLITES AND ZEOLITES SYNTHESIZED FROM FLY ASH DERIVATIVE

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## ABSTRACT

The study serves to investigate two waste materials, namely Acid Mine Drainage and Fly Ash and to recover the solid residues for conversion into an adsorbent that treats brine. The solid residues were then converted into zeolite P through low temperature hydrothermal treatment. The adsorption capacity of the solid residues, zeolite P derived from the solid residues was compared to the commercial zeolite Y and fresh Arnot fly ash. The quality of the resulting water was assessed using different analytical methods before the reaction with adsorbents and after the reaction. A comparison was done based on the removal efficiency of elements. Zeolite P was successfully synthesized from solid residues as confirmed by XRD, BET and FTIR. Brine treatment with fly ash, solid residues, zeolite P and commercial zeolite Y adsorbents was done concentrating on the following major elements Na, K, Mg, Ca and Si. Zeolite P had higher or similar removal efficiency than the commercial zeolite Y for the following elements K, Ca and Mg. Fly ash is the only adsorbent that managed to reduce the concentration of Na in brine and also had a good removal efficiency of Mg. Si leached out of all the adsorbents. This may be ascribed to Si being the major component which dissolved under the conditions tested. Overall, zeolite P did not completely remove the major elements, especially for Na, but did result in a cleaner waste stream which improved brine processing.

**Keywords:** Fly Ash, Neutralization, Zeolites, Acid Mine Drainage, Brine

## 1. INTRODUCTION

Brine is water saturated or nearly saturated with salt. Natural brines are waters with very high to extremely high concentrations of dissolved constituents-elements, ions, and molecules. Brines are also considered to be those waters more saline, or more concentrated in dissolved materials, than sea water (35 grams of dissolved constituents per kilogram of sea water). Brine can contain salt concentrations more than five times greater than the salt content of average sea water. Its disposal poses a serious threat as it could negatively affect the surrounding environment. The disposal of brine is costly because of its composition and due to the large volumes to be handled (Vavra *et al.*, 2004; Al-Agha *et al.*, 2005). Recycling and reuse of water from industrial processes is of vital importance for economic reasons, especially when the industry is using large amounts of water and they also have to comply with the effluent standard limits imposed by environmental regulations. Some industrial wastewaters can contain high heavy metal content, especially those related to the processing of mine ores and from metal industries. However heavy metal removal from wastewater is extremely important because of their toxic effects on aquatic species that are located in receiving water bodies.

According to Gazea several methods are available for the treatment of acid mine waters which vary upon the volume of the effluent, the type and concentration of contaminants present. An effective treatment should be able to neutralise the effluent to a near or neutral pH, lower acidity and to reduce sulphate levels, iron and other metals down to environmentally acceptable limits. The treatment option must also be affordable or reasonably of low cost, easy to install and maintain, be able to produce limited quantities of by-products and recover at least 80% of the feed water. The conventional mine drainage treatment systems involve neutralisation by addition of alkaline chemicals such as limestone, lime, sodium hydroxide, sodium carbonate or magnesia to water (Gazea *et al.*, 1996). Modern society has become reliant on electricity as a source of power. South Africa, specifically in the Mpumalanga and Gauteng provinces possesses a large number of coal-fired power stations for power generation. The principle of a coal-fired power station involves burning of large quantities of coal to produce the electricity needed. Fly ash is a by-product formed as a result of coal burning in power plants. South African fly ash has a high alkalinity and therefore can be evaluated in wastewater treatment to precipitate heavy metallic ions. High capacity adsorbents such as zeolites are also used for brine or saline water treatment as the ion exchange material (Petrik *et al.*, 2005). Acid Mine Drainage (AMD) is characterised by high concentrations of dissolved heavy metals and sulphate, and can have pH values much lower than 2 (Feng *et al.*, 2000). When untreated AMD is discharged into public streams and rivers it pollutes the receiving streams and aquifers and can have detrimental effect on aquatic plant and fish life and the overall effect on streams and waterways can be very

dramatic (Gazea *et al.*, 1996). In the worst-case scenario, all aquatic life virtually disappears; river bottoms become coated with a layer of rust like particles (Gazea *et al.*, 1996).

At the University of Western Cape (UWC), an investigation was carried out on the neutralization of AMD using fly ash (FA) and also to synthesize zeolites from FA and AMD (Somerset, 2003; Klink, 2003). Zeolites of very high purity are always necessary for different applications. Waste materials or waste products including fly ash, can also be used as raw materials for the synthesis of zeolite-containing materials, for many purposes. Fly ash generated from coal-fired power stations is a fine silt-sized powder that contains many unburnt residuals. Some of the main components of fly ash are silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>). These are present in similar chemical ratios to that required for zeolite formation, and therefore fly ash can be used as a raw material for synthesizing zeolites (Lin and Hsi, 1995). Fly ash from brown coal (as burnt in South Africa) proves advantageous for the synthesis of zeolite-containing products in that it is already thermally treated during the combustion process. After the combustion process some silica and alumina contained in the ash already exists in an activated form. Kaolin particles in the coal are converted into metakaolin that can then be easily transformed into zeolites (Stamboliev *et al.*, 1985).

## **2. MATERIALS AND METHODS**

### **Acid Mine Drainage and Fly Ash**

The acid mine drainage (AMD) was obtained from a South African coal plant. The AMD was stored in high density polyethylene (HDPE) containers and refrigerated at 4°C until used for experimental purposes. Fly Ash was collected from the ash disposal sites at a South African Power Station and sealed tightly in a plastic bag (Balfour *et al.*, 2008).

### **Formation of the Solid Residues**

Solid residues were formed by the neutralisation of AMD with fly ash at a fly ash: AMD ratio of 1:3.5. 350ml of AMD was poured in a beaker and the pH and EC were recorded. Subsequently, 100g of fly ash, corresponding to the pre-determined fly ash: AMD ratio required for the experiment was mixed with the AMD. The mixture was stirred with an overhead stirrer, fitted with stainless steel 6-blade paddle impellers. The measurement of EC and pH of the reaction mixture was taken at regular time intervals, until a pH of 7 was obtained. The mixture was then filtered with a 0.45µm cellulose nitrate filter paper on a Büchner filtration system. The filtrate collected was stored in a high density polyethylene container at 4°C. The neutralisation solids residues recovered were dried in an oven at 70°C and stored in an air tight high density polyethylene container, before being used as the starting material for the synthesis of zeolites.

### **Synthesis of Zeolite P**

The synthesis of zeolite P from the solid residues was done using a two step process method, namely ageing followed by hydrothermal synthesis. In a typical synthesis

20 g NaOH and 20 g co-disposed solids were weighed and 100 ml of ultra pure water was used to dissolve the NaOH. Ageing was done under stirring for 48h on a hotplate fitted with a stirrer in a sealable plastic bottle containing the slurry and the temperature of the slurry was kept around 48 °C. Stirring speed was kept between 750 and 1000rpm. After ageing, 150 ml ultra pure water was added to the aged slurry and the slurry was transferred to Parr-bombs and placed in the oven at 100 °C for hydrothermal synthesis. Samples were taken out every 24h and were washed and filtered. The molar composition of this synthesis gel was Si: 3.3 Na: 3.3 OH: 0.6 Al: 90.8 H<sub>2</sub>O. The product formed was analyzed by XRD, XRF, nitrogen BET and FTIR (Sonqishe, 2009).

### **Brine and Co-Disposed Solid Residues; Fly Ash; Zeolite P and Commercial Zeolite Y**

Brine was collected from a coal power plant in the Gauteng province, South Africa. The brine was produced from Lethabo Power station process plant. Ratio 1:3 (adsorbent : brine) was used for this reaction where 1g of an adsorbent (co-disposed solids, fly ash, zeolite P and commercial zeolite Y) was added 30ml of brine in a reaction flask and the reaction time was 60 minutes. pH and EC changes were monitored after five-minute intervals throughout the 60 minutes contact time. After 60 minutes the reaction was stopped and reaction mixture filtered through Whatman No.1 where the filtrate was diluted with deionised water to desired EC, acidified and refrigerated for trace metal analysis. The dilution factor for brine was later used to calculate concentration of brine in the results.

### 3. RESULTS AND DISCUSSION

#### Brine Composition

The initial composition of the brine, prior to the contact with adsorbent is provided in Table 1. The initial pH and EC of brine was 7.8 and 15.83 mS/cm, respectively. The major component is Na with a concentration of 4719 mg/l. The other major elements are Mg, Ca, K and Si in the range of 40 mg/l to 200 mg/l. The minor and trace elements present in brine are B, Al, P, Fe, Sr, Li, Ti, Cr, Mn, Ni, Cu, Zn, Mo, Ba and Pb (concentrations ranging between 5 mg/l and 0.1 mg/l). The following elements were below detection limits in the brine: Be, V, Co, As, Se and Cd (Sonqishe, 2009).

Table 1. Initial concentration of the brine.

Element	Concentration (mg/l)	Element	Concentration (mg/l)
Na	4719.1	Mg	198.4
K	114.7	Ca	112.0
Si	42.6	Sr	4.8
Fe	3.3	Al	2.8
B	1.6	P	1.6
Li	0.5	Cu	0.5
Ni	0.4	Cr	0.4
Mn	0.4	Ti	0.3
Zn	0.2	Mo	0.1
Ba	0.1	Pb	0.1

#### Zeolite P Synthesis

Fly ash generated from coal-fired power stations is a fine silt-sized powder that contains many unburnt residuals. Some of the main components of fly ash are SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> as seen in Table 2. These are present in similar chemical ratios to that required for zeolite formation, and therefore fly ash can be used as a raw material for synthesizing zeolites (Lin and Hsi, 1995). Zeolite P is formed in a chemical system containing the following species: CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O. As can be seen from Table 2 the solid residue provides the chemical environment required for the formation of zeolite P.

Table 2. The XRF analysis of the fly ash, synthesized solid residues and the zeolite P synthesized from the co-disposed solid residues.

Major element	Concentration (wt %)		
	Fly ash	Solid residues	Zeolite P
Si (as SiO <sub>2</sub> )	53.4	45.88	37.56
Al (as Al <sub>2</sub> O <sub>3</sub> )	23.4	24.57	25.77
Ti (as TiO <sub>2</sub> )	1.34	1.195	
Fe (as Fe <sub>2</sub> O <sub>3</sub> )	4.72	6.308	5.60
Mn (as MnO)	0.06	0.1	0.12
Mg (as MgO)	2.70	2.39	2.38
Ca (as CaO)	8.43	7.145	8.61
Na (as Na <sub>2</sub> O)	0.35	0.407	7.61
K (as K <sub>2</sub> O)	0.49	0.513	0.07
P (as P <sub>2</sub> O <sub>5</sub> )	0.35	0.679	0.22
S (as SO <sub>3</sub> )	4.5	3.477	0.40
Cr (as Cr <sub>2</sub> O <sub>3</sub> )	0.03	0.037	
Ni (as NiO)	0.01	0.011	
H (as H <sub>2</sub> O)		1.154	
Loss on ignition	2.36	5.141	11.31

Zeolite P was synthesized using a method which consisted of two steps: a pre-treatment, called the ageing step, and a mild hydrothermal treatment at 100°C. The ageing period of the gel solution is important to obtain the desired crystalline phase and to accelerate crystallization (Ertl *et al.*, 1997). The ageing process must be carried out at room temperature or at a slightly increased temperature, remaining below the temperature of the thermal treatment (Barrer, 1982). During the ageing phase, there is a partial monomerisation of the silica particles catalysed by the hydroxyl ions.

This induces an increase of monomeric silica in the liquid phase, which is then available as feedstock for the hydrothermal treatment.

The mild temperature synthesis at 100°C resulted in a solid product containing zeolite P, quartz and mullite (Figure 1). The pore size of zeolite P is smaller than that of faujasite, and is defined by an 8 membered ring. As a result of this difference in pore size, zeolite Y is a more favoured configuration for adsorption as it can accommodate a greater amount and variety of elements. However, zeolite P is well known and frequently used as adsorbent and ion-exchange material. Mullite has a dense orthorhombic structure. Its framework consists of alternating octahedrons of Al and tetrahedrons of Si. Mullite could form during a thermal treatment at 100°C (Kong, 2003), but in this experiment its presence represented the unconverted mullite phase from the original fly ash.

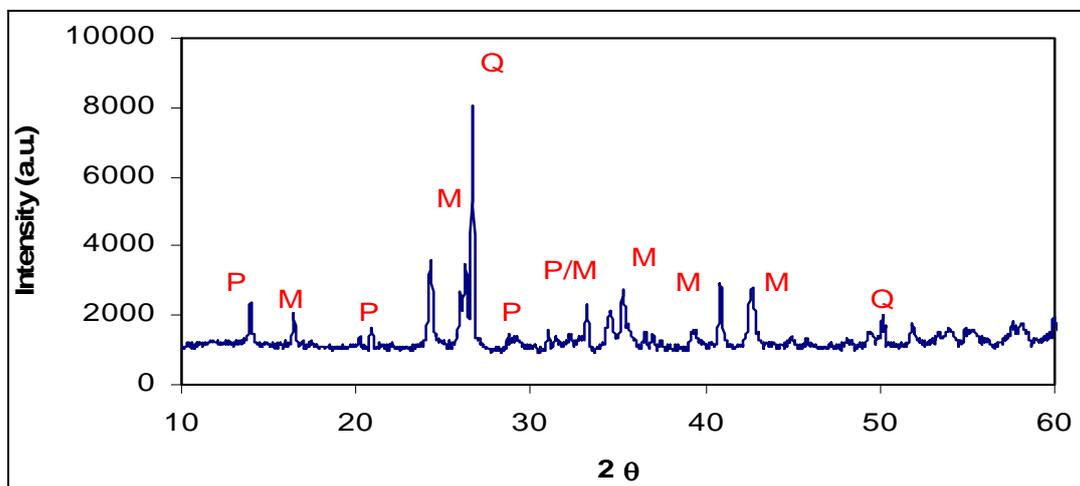


Figure 1. X-ray diffraction spectra of zeolite P synthesis after 48 hours at 100°C (P = zeolite P, M = Mullite, Q = Quartz).

The FTIR spectra (Figure 2) of the washed product showed a sharp peak at 1000  $\text{cm}^{-1}$ . This peak is characteristic of the formation of linear molecules and polymers of silicate, according to the FTIR spectroscopy assignments of silicate species given by Bass and Turner (Bass and Turner, 1997). Moreover the zeolite structural framework bands appear to be fully formed in the region below 700  $\text{cm}^{-1}$ . From the spectra, 48h of hydrothermal treatment was found to be sufficient for the crystallization of the zeolite crystalline framework. Upon inspection of the difference between unwashed and the washed solids spectra, the peak at about 1500  $\text{cm}^{-1}$  in unwashed solids indicates that there are soluble species, which could be leached that remain incorporated in the solid.

The third indication that a microporous zeolite P is formed is the increase in the nitrogen BET surface area from 1-2  $\text{m}^2/\text{g}$  for fly ash to 61  $\text{m}^2/\text{g}$  for the zeolite P synthesized from the co-disposed solid residues. The increase in surface area is not as high as would be expected if this were a pure zeolite P phase, and the XRD shows that other phases present included quartz and mullite (Sonqishe, 2009).

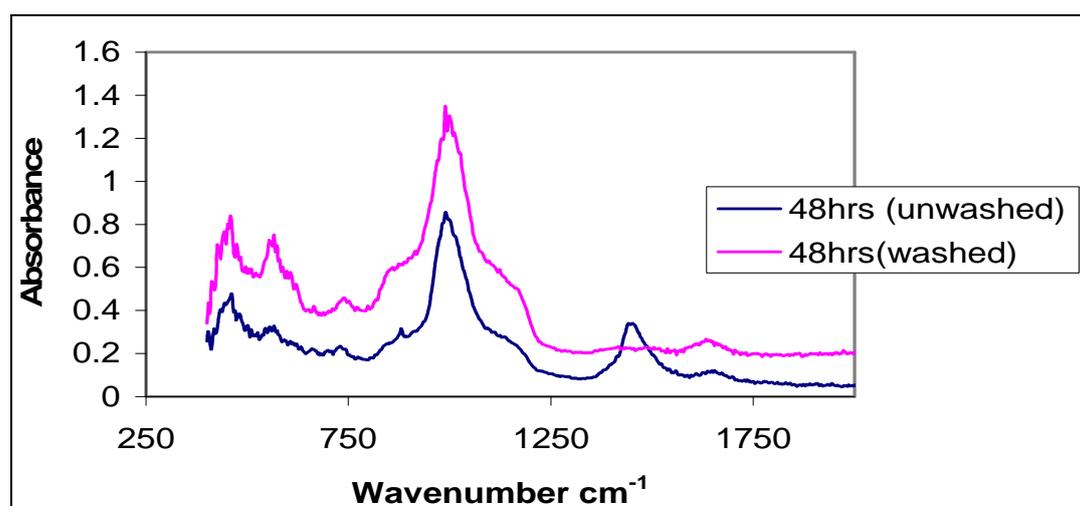


Figure 2. Infrared spectra of product synthesised from solid residues after 48h of thermal treatment at 100°C (Balfour *et al.*, 2008).

## Brine Treatment with Fly Ash, Zeolite P, Solid Residues and Commercial Zeolite Y

The focus on the results was on the major ions as referred to on the text being Na; Ca; K; Mg and Si as they are regarded as the major constituents of brine.

Figure 3 gives the pH and EC changes with time when the brine was treated with the different adsorbents. As shown in Figure 3, the pH remained constant throughout the reaction time. However EC seemed to have increased slightly even though the change was not much. The slight decrease in the EC can be attributed to the adsorption of the elements onto the adsorbents.

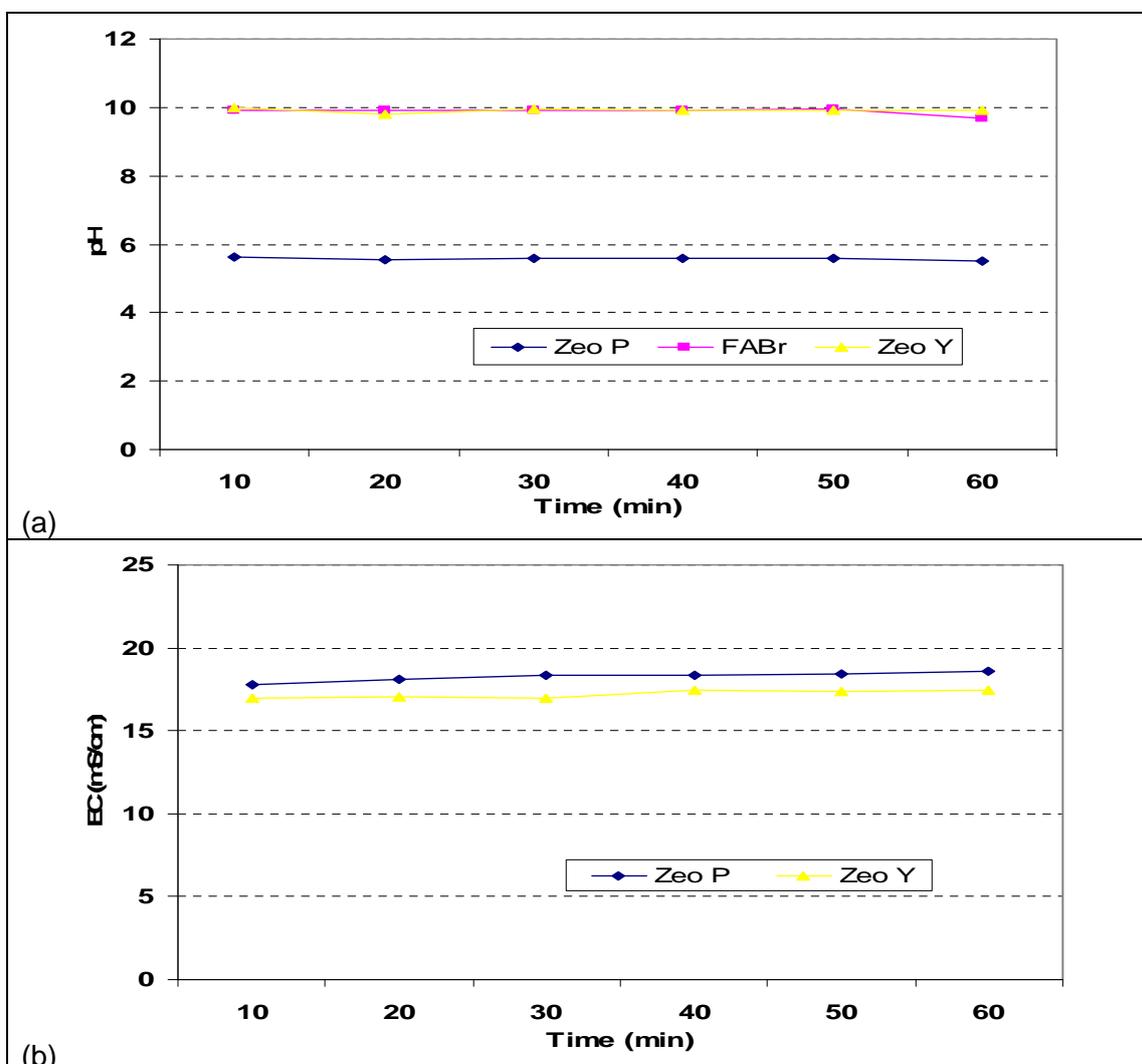


Figure 3. The (a) pH and (b) EC changes of the brine treatment with different adsorbents at a 1:3 adsorbent: brine ratio

Fly ash seemed to have a better Na removal efficiency (23%) followed by zeolite Y and co-disposed solids with removal efficiencies of (21%) and (7%) respectively, whereas for other adsorbents Na is seen to leach. However, the amounts leached out were very small. The low removal of Na could be ascribed to the high Na concentration in the brine and to the fact that Na is exchanged out of the zeolites during the uptake of more problematic species.

For Si, the removal efficiency is not very good for all the adsorbents used, instead it leaches out in zeolites P and commercial zeolite Y and fly ash which could be because according to the XRF analysis, Si is one of the major components of all the adsorbents used in the reactions. Co-disposed solid residues have higher removal efficiency compared to other adsorbents. The leaching was significant for the commercial zeolite Y, zeolite P and the fly ash.

Ca was successfully removed by the commercial zeolites and the zeolite P but leaching was observed for the fly ash and solid residues. Zeolite P removal efficiency (60%) and zeolite Y removal efficiency (76%) had a good removal efficiency except synthesized solids and fly ash where they leached out of the adsorbent instead. South African fly ash has a high percentage of CaO in its composition (Table 2). This CaO is in the amorphous phase and may be dissolved and leached in to the brines. However co-disposed solid residues are a by-product of fly ash that explains why Ca would leach out of it as well. The commercial zeolite Y does not contain Ca in its framework and therefore no leaching was

observed. Zeolite P does have Ca in it but this Ca may be incorporated in the framework or tightly associated with acid site and therefore did not leach out into the brine and in fact adsorption of the Ca onto zeolite P was observed.

All the adsorbents investigated have a good removal efficiency for Mg except for the solid residues and fly ash removal efficiencies of (12%) and (29%) respectively. The highest removal efficiency was obtained by the zeolite Y (76%).

Commercial zeolite Y for the removal of K it can be seen that there is a better removal efficiency (45%). Zeolite P and fly ash had good removal of K from the brine (34%) and (35%) respectively. Co-disposed solid residues also have a good removal efficiency of (22%) as well. There was no leaching of K from adsorbents into brine.

#### **4. CONCLUSIONS**

Zeolite P was successfully synthesised from the solid residues as confirmed by XRD and FTIR.

However, a pure zeolite P phase was not obtained as was identified by XRD. Quartz and mullite are also present resulting in a mixed crystalline and amorphous solid phase. Fly ash seemed to have better removal efficiency for compared to all other adsorbents. The low removal of Na could be ascribed to the high Na concentration in the brine and to the fact that Na is exchanged out of the zeolite during the uptake of more problematic species. Significant Si leaching was observed from the commercial zeolite Y, zeolite P and fly ash. Si is the major component of these adsorbents and this could indicate some dissolution of these adsorbents under the conditions tested.

Commercial zeolite Y and zeolite P had good removal of Ca whereas fly ash and solid residues leached Ca. In the fly ash and solid residues this may be due to the high CaO present in the amorphous phase which can be readily dissolved into the brine.

Zeolite P had higher or similar removal efficiency than the commercial zeolite Y for the following elements K, Ca and Mg. Overall, zeolite P did not completely remove the major elements, especially for Na, but did result in a cleaner waste stream which improved brine processing. The effect of adsorption time was complex due to the complexity of the brine and competitive adsorption between the different elements. A high adsorbent: brine ratio is required for brine treatment. The zeolite P did not completely remove all the major elements from the brine and this is especially true for Na. However, the zeolite P did “clean up” the brine sufficiently to simplify the brine and allow for easier and less expensive further treatment of brine, since this was a pre-treatment step before desalination using reverse osmosis.

Table 3. Removal of elements from brine with fly ash, zeolite P, solid residues and commercial zeolite Y (ratio of 1:3 absorbent: brine, and after 60 min contact time).

Elements	Brine Conc. (mg/l)	Treatment with Zeolite P		Treatment with Zeolite Y		Treatment with Co-disp.		Treatment with Fly ash	
		Residual Conc. (mg/l)	Removal Effeciency (%)	Residual Conc. (mg/l)	Removal Effeciency (%)	Residual Conc. (mg/l)	Removal Effeciency (%)	Residual Conc. (mg/l)	Removal Effeciency (%)
<b>Na</b>	4603.55	4982.70	Leaching	3652.11	21	4295.59	7	3538.02	23
<b>Mg</b>	209.22	84.18	60	69.26	67	183.28	12	147.63	29
<b>Ca</b>	135.79	54.30	60	33.13	76	468.45	Leaching	216.99	Leaching
<b>K</b>	126.86	83.85	34	69.43	45	99.19	22	82.10	35
<b>Si</b>	48.89	70.72	Leaching	96.01	Leaching	40.11	18	67.71	Leaching

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