Ultrasonic assisted synthesis of zeolite A from coal fly ash using mine waters (acid mine drainage and circumneutral mine water) as a substitute for ultra pure water

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Abstract The current study is focused on synthesis of single phase zeolite A from South African coal fly ash using mine water as a substitute for ultra pure water. Initially, synthesis conditions for preparing zeolite A were optimized using ultra pure water and there after ultra pure water was substituted with raw, untreated mine waters (acid mine drainage and circumneutral mine waters). The effect of ultrasound during the aging step prior to hydrothermal synthesis was also investigated and it was found that sonication reduced the synthesis time of pure zeolite A to one hour.

Key Words Zeolite A, fly ash, ultra pure water, acid mine drainage, circumneutral mine water.

Introduction

Coal mining and combustion for electricity generation presents serious environmental problems due to the resulting waste. Mining of coal leads to production of large volumes of mine waters that can be either acidic, circumneutral and/or alkaline, while the coal combustion process generates massive amounts of fly ash. Safe and efficient disposal or re-use of these two types of waste (mine waters and fly ash) is therefore an ongoing challenge to industrial and academic researchers. There are many different ways proposed for recycling coal fly ash (Ahmaruzzaman 2010). For instance, zeolites synthesis from fly ash has been proposed as an attractive alternative for this purpose (Querol 2002) due to the potential economic and environmental benefits. Different technlogies have also been proposed and implemented to treat mine waters but the associated cost makes them unattractive. More research is therefore still needed to find other cost-effective alternatives for either treatment or re-use of mine waters. Some researchers have proposed co-disposal of both wastes as a way of ameriolating each other by using of fly ash to remove sulphates from mine waters (Gitari 2006; Madzivire 2010). Other studies have also shown that zeolites can be synthesized from solid residues collected after the co-disposal reaction of fly ash and mine water (Somerset 2008). These studies resulted in the synthesis of mixed phases of zeolites which showed low potential for industrial applications. The current research seeks to investigate the use of mine waters to directly synthesize single phase zeolite A from fly ash. Zeolite type A, denoted by the International Zeolite Association (IZA) code system as Linde Type A (LTA), is classified into three subgroups based on the type of exchangeable cations present in its structure. These subgrouping include; potassium exchanged form, K-LTA or Linde 3A, sodium exchanged form, Na-LTA or Linde 4A and calcium exchanged form, Ca-LTA (Linde 5A; Montanari and Busca 2006). Zeolite A is of great commercial importance due to its molecular sieving and ion exchange properties. In this study the use of ultrasound has been employed to enhance the dissolution of fly ash in mine water and boost the crystallization process.

Experimental methodology

Materials and Characterization techniques

Coal fly ash from a South African coal-fired power plant was used as the synthesis feedstock. Sodium aluminate (Riedel-De-Haen AG) and sodium hydroxide (Merck) were used as the additional aluminium and sodium sources for the zeolite preparation mixture, respectively. Mine waters, acid and circumneutral, were collected from two coal mines found in South Africa. Qualitative and quantitative X-ray diffraction (XRD) analyses of fly ash were perfomed using a Philips X-ray diffractometer and PANalytical X'Pert Pro powder diffractometer respectively. Chemical composition analysis was conducted using a Philips PW 1480 X-ray spectrometer. Hitachi X-650 scanning electron microanalyser was used for morphological analysis. The concentrations of ionic species in the mine waters was measured by the use of inductively coupled plasma atomic emission (ICP-AES) spectrometer. A Perkin Elmer spectrum 100 FT-IR Spectrometer was used to provide information about molecular structure of the synthesis product. Measurement of pH was done using a HANNA HI 991301 portable pH/EC/TDS/temperature meter.

Synthesis procedure

Zeolite A was synthesized by fusing fly ash with sodium hydroxide followed by a hydrothermal reaction. A homogenous mixture of fly ash and

sodium hydroxide was prepared by mixing fly ash and sodium hydroxide in a ratio of 1 : 1.2. The resultant mixture was fused at 550 °C for 1.5 hours. Thereafter, the fused fly ash was cooled, ground and thoroughly mixed. During the synthesis, 10g of the fused fly ash was mixed with 50 ml of ultra pure water and stirred for two hours. On the side, a solutions of sodium aluminate were prepared by mixing sodium aluminate powder with sodium hydroxide in a ratio of 1 : 2 and stirred using a magnetic stirrer for 30 minutes. 20 ml of the sodium aluminate solution was added to the fly ash slurry and stirred for another ten minutes. The purpose of the addition of the aluminate solution was to control the molar ratio of the fly ash slurry for the subsequent synthesis of a single phase zeolite A. The resulting slurry was then subjected to crystallization at 100 °C by varying the reaction time. A different set of experiements were conducted whereby the fly ash slurry was filtered before addition of extra Al to get a clear solution that was used for sythesis. After the hydrothermal crystallization, the solid crystalline product was recovered by filtration and was washed thoroughly till the filtrate reached pH 9—10 and dried at a temperature of 100 °C for 12 hours. It is important to point out that initially synthesis conditions for preparing zeolite A were optimized using ultra pure water and there after the ultra pure water solvent was substituted with raw, untreated mine waters (acid mine drainage and circumneutral mine waters).

Results and discussion

Table 1 presents the major elemental composition of the raw fly ash. The analysis was done in triplicate. The average SiO_2/Al_2O_3 ratio of fly ash was found to be 1.65 which was a good indicator for the potential of synthesis of zeolites.

Qualitative and quantitative XRD of raw fly ash presented in Figure 1 show that the predominant phases were amorphous glassy Si, quartz, mag-

Table 1 *Major elemental composition of fly ash.*

Major Oxide	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3	LOI	Sum
Average mass %	50.91	30.91	3.46	0.02	1.48	6.2	0.1	0.6	1.65	0.56	0.24	3.85	99.99
Std dev	0.18	0.14	0.03	0.00	0.02	0.02	0.01	0.01	0.01	0.02	0.00	0.19	0.00
SiO_2/Al_2O_3 ratio	1.65												

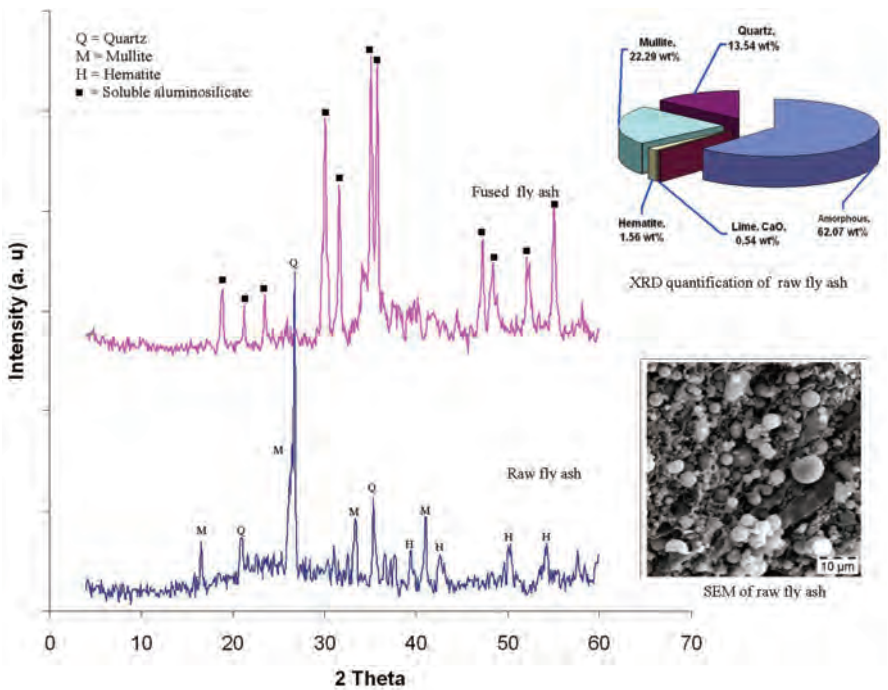

Figure 1 *XRD patterns of raw and fused fly ash: Inset: Quantitative XRD analyis and SEM of raw fly ash.*

netite, and hematite. All of these phases were tranformed to a soluble aluminosilcate phase after fusion with NaOH.

Elemental composition of mine waters

The pH for circumneutral water and acid mine drainage was found to be 6.5 and 2.5 respectively. Comparing the compositions of the two waste waters (Table 2), it is evident that circumneutral mine water had a high concentration of Na and SO_4^{2-} meaning that it could be classified as Na-rich mine water while acidic mine water had a high concentration of Fe, Ca, Mg, K and Mn but with low concentration of SO_4^{2-}.

Optimization studies using ultra pure water

Studies on optimisation of synthesis conditions for zeolite A (results not presented here) were conducted by investigating the effect of Si/Al ratio, hydrothermal crystallization time and temperature using ultra pure water as a solvent. The best conditions for synthesis of a single phase zeolite A without the use of ultrasound were found when Si/Al ratio was 0.68 with hydrothermal crystallization temperature of 100 °C for 2 hours.

Substitution of ultra pure water with mine waters

The XRD results of substitution of the ultra pure water solvent with raw, untreated mine waters (acid mine drainage and circumneutral mine waters) are presented in Figure 2. The pattern obtained when synthesis was conducted at 100 °C for 2 hours using circumneutral mine water compared with that of using ultra pure water does not show noticeable differences. It can be derived that the presence of extra elements in the circumneu-

Table 2 *Composition of the mine waters.*

Element (ppm)	Na	Ca	Mg	K	Mn	B	Sr	F	SO_4^{2-}	Cl
Circumneutral mine water (CNW)	886.58	70.35	39.54	9.94	0.01	2.61	2.05	0.06	1475.25	24
Acid mine drainage water (AMD)	70.48	598.73	398.9	34.16	88.22	0.09	1.02	8158.2	42862	9.8

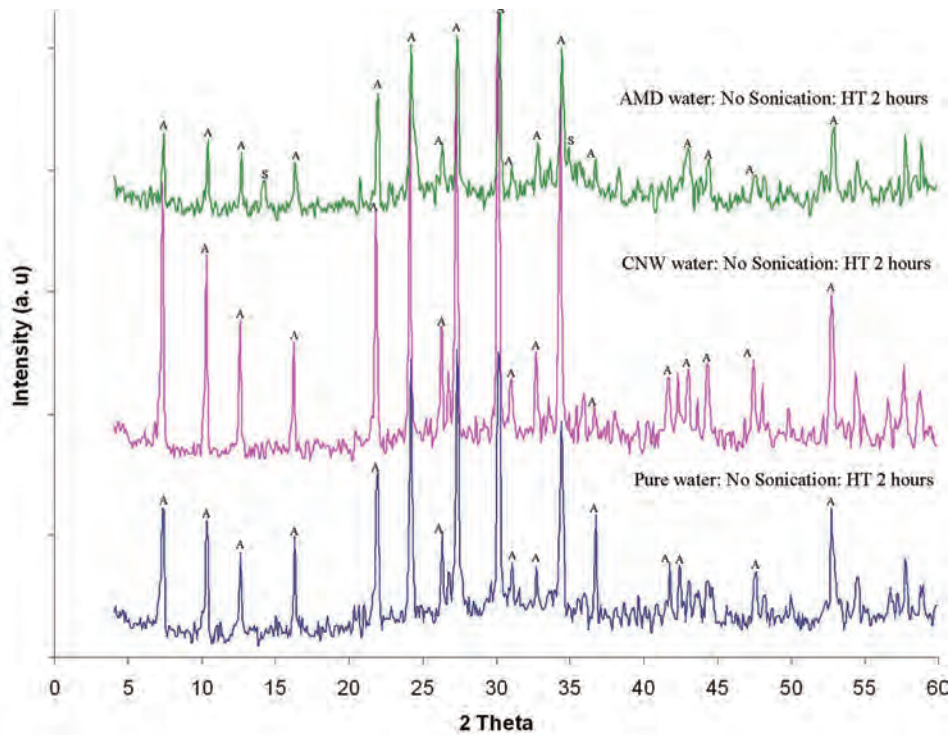

Figure 2 *XRD patterns of zeolites synthesized by substitution of ultra pure water with acidic (AMD) and circumneutral (CNW) mine water.*

tral mine water did not interfere with the crystallization process since the same single phase was obtained. When acid mine drainage was used as solvent during the synthesis process, a new phase (hydroxysodalite) which in this case can be referred to as a contaminant was observed to be formed. This can be explained by the presence of a high Ca concentration which is known to have zeolite structure breaking property (Catalfamo 1997).

Effect of sonication before hydrothermal crystallization

The best results that had been obtained without the application of ultrasound had shown that a single phase zeolite A formed when crystallization was conducted at 100 °C for two hours. Figure 3 shows that crystallization time was reduced to one hour upon application of ultrasound instead of normal stirring prior to the hydrothermal crystallization step. Cavitation phenomenon (Mason 1997) which is known to leads to acoustic cavitations (bubble formation) and subsequent implosion has been reported to induce the stirring effect in a solution due to the microjetting and microstreaming of the collapsed bubbles (Lindley 1992) and this is assumed to be the major contributing factor in the enhancement of fly ash dissolution. Earlier studies conducted by Feng (2004) had also reported that dissolution of fly ash could be enhanced by the application of ultrasound.

Morphological analysis: SEM analysis

The SEM analysis of zeolite A obtained when fly ash slurry was sonicated prior to hydrothermal synthesis using ultra pure water, circumneutral mine water and acid mine drainage as well as that obtained using a clear solution of the same solvents is presented in Figures 4 and 5 respectively. The typical cubic shaped crystals of zeolite A were observed in all the images. There was no observable difference in the morphology of zeolites obtained when circumneutral mine water was used as solvent compared to that obtained using ultra pure water. On the use of acid mine drainage, some round "fluffy" particles could be observed and this were thought to be the traces of hydroxylsodalite phase that was earlier identified by XRD analysis. Comparing the SEM images of synthesis products from raw fly ash slurry with that from a clear solution, it can be seen that synthesis using a clear solution gave a much higher quality zeolite A since most of the product was crystalline. It was interesting to note the application ultrasound to the synthesis slurry of zeolite A synthesized using acid mine drainage led to a decrease in the particle sizes and the reason for this behavior could not be explained at this moment.

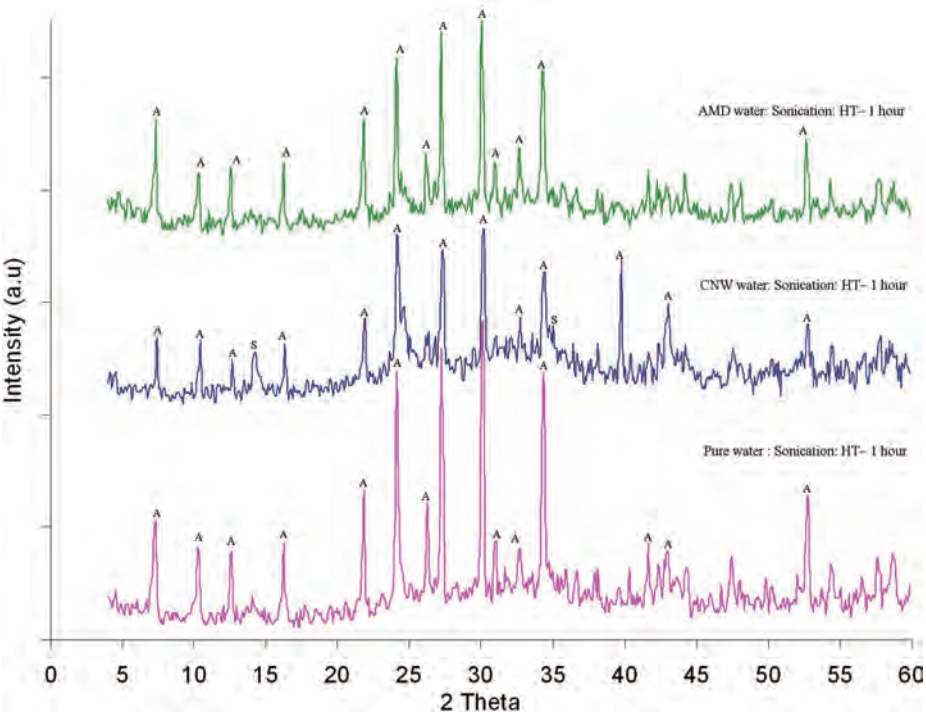

Figure 3 *XRD comparison of zeolite samples synthesized using UP water, CNW and AMD mine waters synthesized from the raw fly ash slurry.*

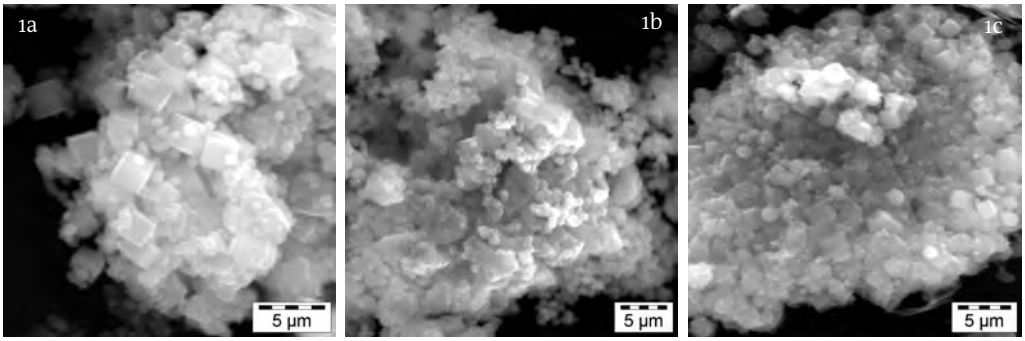

Figure 4 *SEM images of zeolite A synthesized using different solvents 1a) pure water, 1b) CNW and 1c) AMD with sonication at 100 °C for one hour using raw unfiltered fly ash slurry.*

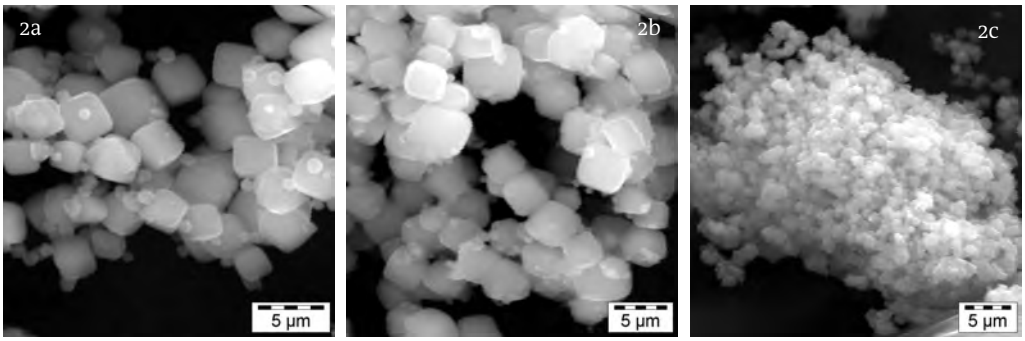

Figure 5 *SEM images of zeolite A synthesized using different solvents 2a) pure water, 2b) CNW and 2c) AMD with sonication at 100 °C for one hour using a clear synthesis solution.*

FTIR Analysis

The FTIR analyses of synthesis products obtained by substitution of ultra pure water with mine waters is shown in Figure 6. Typical characteristic infrared bands associated with zeolite A which were reported by Rayalu (2005) as: asymmetric stretching of T–O bond 1000—1500 cm^{-1}, symmetric stretching of T–O bond 660 cm^{-1}, bending vibration of T–O bond 464 cm^{-1}, D4R rings 560 cm^{-1}. The degree of crystallinity of fly ash derived zeo-

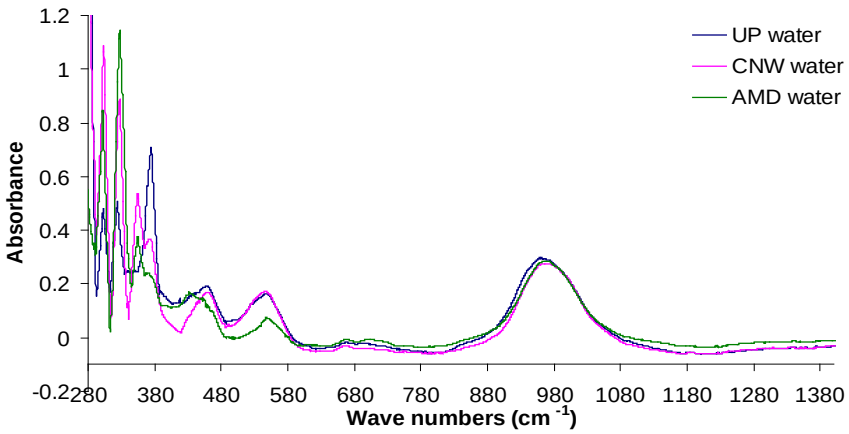

Figure 6 *Comparison of spectra of zeolite synthesized using different synthesis solvents (UP water, CNW mine water and AMD mine water).*

lites which was also studied by Rayalu (2005) by comparing the ratio of intensity of the peak at 560 and 480 cm^{-1} with the corresponding ratio for a standard sample will be conducted at a later stage.

Conclusions

The results obtained showed that it was possible to obtain a single phase zeolite A using untreated circumneutral mine water (CNW) which was the same as that obtained when ultrapure water was used during synthesis. When acid mine drainage water (AMD) was used to synthesize zeolite A an almost single phase zeolite A was obtained but with trace "contaminants" of hydroxysodalite. This finding proved that it is not only possible to ameliorate the waste (fly ash and mine waters) but useful products (zeolites) could also be obtained. The effect of ultrasound during the ageing step prior to hydrothermal synthesis was found to reduce the synthesis time of single phase zeolite A from two hours to one hour and also enhanced the crystallization process.

Acknowledgements

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