Controlled Release Zeolite Fertilisers: A Value Added Product Produced from Fly Ash

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ABSTRACT

Of 13 million tones of coal ash produced in Australia in 2003, only 34% is used in some way, with only 15% utilised in applications of value[1], while the remainder is accumulated in landfills and ash dams. This low level of ash utilisation is inevitable due to the combination of inherently high transport costs, and relatively low value products. This situation argues for more value-added utilisation of coal ash to overcome the transport cost barrier. Zeolite synthesised from fly ash for agricultural application as a controlled release fertiliser, is a technology which offers considerable advantages in terms of economic, technical and environmental performance. The Australian fertiliser market consumed 192 Kt of potassium (K) in 1999[2]. Assuming a cation exchange capacity of 3.5, this market is equivalent to 1.5 Mt of zeolite per annum, requiring roughly an equivalent amount of fly ash to produce. With Muriate of Potash (KCl, 60% K₂O equivalent) selling for $AU395/tonne in 2002[3], this fertiliser market is both a high value and high volume market, with the potential to consume significant quantities of fly ash. Studies using natural zeolites have demonstrated significant improvements in fertiliser efficiency for zeolites compared to soluble salts (Clinoptilolite is 7 – 9 times more efficient than KNO₃ in potting medium[4]). This paper examines the hydrothermal process for producing zeolites (such as Analcime, Cancrinite, Chabazite, Gismodine, and Gmelinite) from coal fly ash, including the relationship between zeolite types produced and operating conditions, desirable zeolite properties for controlled release fertilisers, optimal production conditions, and economic implications.
1 BACKGROUND

The utilisation of fly ash from coal-fired power plants is at present realised by low technology applications such as in cement, and construction materials (including mine backfills, soil stabilisation, engineered fills, and road base). However, ca. 500 million tonnes of coal ash is produced globally each year, with only 20% effectively utilised\[^5\], with 13 million tonnes of coal ash currently produced in Australia each year, of which 34% was effectively utilised, and only 15% utilised in applications of value in 2003\[^1\] see Figure 1. The remainder is accumulated in landfills and ash dams, causing considerable adverse environmental effects and public concerns.

This low level of ash utilisation is inevitable due to the inherent high transport costs for the relatively low value products produced, especially in Australia where a small population is spread over a large area. This makes it difficult for ash to compete with alternative raw materials. Low value beneficial strategies have proven capable of utilising significant quantities of fly ash in the short term, but incapable of maintaining this in the long term. The cement market is close to saturation\[^6\], it will continue to grow, but is incapable of any major increase in its use of fly ash. This situation argues for the increased diversification of exploited utilisation strategies, in particular, more value-added high technology utilisation of fly ash as an effective means to overcome the transport cost barrier. Zeolites synthesised from fly ash is a technology, which offers considerable advantages in terms of economic, technical and environmental performance.

\[\text{Figure 1 : Current state of ash utilisation within Australia; (i) Statistical trends grouped according to value, reproduced from the ADAA}^{[1]}, \text{ (ii) Strategies available for exploitation have been classified into groups according to their usefulness and processing intensity}\]

\[\text{For non-beneficial use, fly ash is seen as having no value, and is generally an economic burden to the ash producer, eg landfill. In simple utilisation strategies, fly ash is the final product, eg agricultural products, or is blended to form the final product, eg blended cement. In advanced utilisation strategies, fly ash is processed to produce a final product, eg zeolites, or to extract a product from the ash, eg cenospheres.}\]
A significant number of zeolite markets have been identified and classified into groups, see Figure 2 below. Of these markets, agricultural applications offer competitive prices (see Figure 3 below), and have the largest potential market volume for zeolites.

![Figure 2: Classification of different zeolite markets](image)

### 1.1 What is a Zeolite?

Zeolites are alumino-silicate minerals with a structure containing SiO$_4$ and AlO$_4^-$ tetrahedra, linked together with adjacent tetrahedra sharing oxygen to form distinctive crystalline structures (framework structures), contain large vacant spaces (cages) (see Figure 4 below) that can accommodate cations (Na$^+$, K$^+$, Ba$^{2+}$, Ca$^{2+}$), as well as large molecules and cation groups (H$_2$O, NH$_4^+$). The cations are distributed throughout the material and play a charge balancing role with the AlO$_4^-$ tetrahedra.

The cage structures of zeolites are interconnected in three dimensions by channels of constant diameter (see Figure 4 below). Only molecules with a small enough size to pass through channels can enter the internal structure of the zeolite (geometrical selectivity). These void spaces can be filled with water (or other molecules), which can be driven off and reabsorbed without changing the framework structure.

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* Assuming an exchange rate of $AU1 = $US0.75
The charge balancing cations (Na\(^+\), K\(^+\), Ba\(^{2+}\), Ca\(^{2+}\)) can be exchanged with other cations in aqueous solution, without affecting the aluminosilicate framework (see ion exchange capacity in Table 1 below).

Different zeolites have different selectivity for different cations, a strong selectivity for a particular ion will see that ion preferentially exchanged into the zeolite, and the non-selective species preferentially released into solution.

These properties distinguish zeolites as a unique material and are important in its application. For many applications, like controlled release fertilisers, most zeolites will suffice. However not all zeolites were created equal, consequently some zeolites perform better than others for a particular application. Understanding this and knowing how to control the production process to produce the desired zeolite product is critical for the identification and manufacture of a superior product.

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Table 1: Typical properties of some economic zeolites, adapted from Holmes (1994)

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Typical unit cell formula</th>
<th>Framework structure(^{(A)})</th>
<th>Void volume (%)</th>
<th>Specific gravity</th>
<th>Channel dimensions (Å)</th>
<th>Cation Exchange Capacity(^{(B)}) (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analcime</td>
<td>Na(<em>{16})(Al(</em>{16})Si(<em>{32})O(</em>{96})).16H(_2)O</td>
<td>ANA 18</td>
<td>2.24-2.29</td>
<td>2.6</td>
<td>4.54</td>
<td></td>
</tr>
<tr>
<td>Chabazite</td>
<td>(Na(<em>2)Ca(<em>3))(Al(</em>{12})Si(</em>{24})O(_{72})).40H(_2)O</td>
<td>CHA 47</td>
<td>2.05-2.10</td>
<td>3.7×4.2</td>
<td>3.81</td>
<td></td>
</tr>
<tr>
<td>Clinoptilolite</td>
<td>(Na(_3)K(<em>7))(Al(<em>6)Si(</em>{12})O(</em>{36})).24H(_2)O</td>
<td>HEU 39?</td>
<td>2.16</td>
<td>3.9×5.4</td>
<td>2.54</td>
<td></td>
</tr>
<tr>
<td>Erionite</td>
<td>(Na(_2)Ca(_9))(Al(_9)Si(<em>27)O(</em>{27})).27H(_2)O</td>
<td>ERI 35</td>
<td>2.02-2.08</td>
<td>3.6×5.2</td>
<td>3.12</td>
<td></td>
</tr>
<tr>
<td>Laumontite</td>
<td>Ca(<em>3)(Al(<em>6)Si(</em>{18})O(</em>{48})).16H(_2)O</td>
<td>LAU 34</td>
<td>2.20-2.30</td>
<td>4.6×6.3</td>
<td>4.25</td>
<td></td>
</tr>
<tr>
<td>Mordenite</td>
<td>Na(_9)(Al(<em>6)Si(</em>{12})O(_36)).24H(_2)O</td>
<td>MOR 28</td>
<td>2.12-2.15</td>
<td>2.9×5.7</td>
<td>2.29</td>
<td></td>
</tr>
<tr>
<td>Linde A(^{(C)})</td>
<td>Na(_{12})(Al(_2)Si(_2)O(_8)).27H(_2)O</td>
<td>LTA 47</td>
<td>1.99</td>
<td>4.2</td>
<td>5.48</td>
<td></td>
</tr>
<tr>
<td>Linde X(^{(C)})</td>
<td>Na(_{66})(Al(<em>66)Si(</em>{106})O(_364)).264H(_2)O</td>
<td>FAU 50</td>
<td>1.93</td>
<td>7.4</td>
<td>4.73</td>
<td></td>
</tr>
</tbody>
</table>

\(^{(A)}\) Framework structure types are classified according to a capitalised three letter code \(^{(B)}\) Calculated from unit cell formula, \(^{(C)}\) synthetic phases

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\(\text{The framework structure graphic was created using chabazite crystal data}^{[11]}\) and Balls & Sticks\(^{[12]}\) 3D chemical visualisation software
1.2 Cation Exchange and Fertilisers

Cation exchange is a reversible chemical reaction between cations (e.g., plant nutrients $K^+$, $NH_4^+$, $Ca^{2+}$, $Mg^{2+}$) in the solid phase (e.g., zeolite) and in solution (e.g., water in soil). The behaviour of this exchange will depend upon the selectivity of the zeolite.

For a non-selective zeolite, all nutrients are exchanged into the lattice and are released to maintain the same cation ratios in solution as in the zeolite. A dynamic equilibrium occurs where the zeolite behaves as a general ion buffer.

However, by the nature of ion exchange reactions, ion exchangers always exhibit a greater selectivity or affinity for particular ions over others, and have an ordered selectivity sequence for cations.\[13; 14\]

Due to differences in pore size and framework charge, different zeolites have different selectivity for different elements. The selectivity sequences for zeolite NaP1 (GIS) produced from fly ash are listed below; however previous work has not included cations important to agricultural applications. The differences in selectivity may be due to slight variations in the Si/Al ratio of the zeolites produced.

\[Cr^{3+} > Cu^{2+} > Ba^{2+} > Fe^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+}\] \[15\]
\[Pb^{2+} > Sr^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cd^{2+} > Cs^+\] \[16\]
\[Ba > Cu > Cd ∼ Zn > Co > Ni\] \[17\]
\[Fe^{3+} = Al^{3+} ≥ Cu^{2+} ≥ Pb^{2+} ≥ Cd^{2+} = Ti^+ > Zn^{2+} > Mn^{2+} > Ca^{2+} = Sr^{2+} > Mg^{2+}\] \[18\]
\[Cr^{3+} > Zn^{2+} > Pb^{2+}\] \[19\]

Under equilibrium conditions a cation that a zeolite has a high selectivity towards, will have a higher relative concentration (relative to a low selective cation) in that zeolite than in the solution. The relative selectivity between any two cations is usually described by the separation factor ($\alpha_A^B$), Equation 1, or the selectivity coefficient ($K_A^B$), Equation 2 below.

$$\alpha_A^B = \frac{(X_A^B)_Z}{(X_A^B)_Aq} [13; 14]$$

$$K_A^B = \frac{(X_A^B)^{Z_A}}{(X_A^B)^{Z_A}_{aq}} [13; 14]$$

A zeolite loaded with $K^+$ and/or $NH_4^+$, and applied as a fertiliser onto the soil, will result in the exchange of $K^+$ and $NH_4^+$ ions from the zeolite to water in the soil to maintain an equilibrium concentration in the soil. As $K^+$ and $NH_4^+$ are stripped from the soil by plants, more is released by the zeolite to maintain a dynamic equilibrium between the soil and the zeolite. In conjunction with the release of $K^+$ and $NH_4^+$ ions, other ions in the soil, such as $Ca^{2+}$ will be exchanged into the zeolite lattice to maintain charge neutrality (See equations 3 and 4). By removing calcium from the soil system, the
insoluble calcium phosphate is replaced by soluble potassium and ammonium phosphates, making them more available to plants\textsuperscript{[4]}. By having fewer nutrients in solution at any one time, less is lost through leaching, and the efficiency of fertiliser application is improved, see Figure 5 below. By controlling the selectivity of zeolite, the concentration of nutrients in solution can be controlled.

Urea is a nitrogen fertiliser that is very soluble in water, and can be absorbed into dry zeolite when molten and crystallised at 132°C. This nitrogen fertiliser's slow release is controlled by two mechanisms (i) physical encapsulation and (ii) ion exchange of NH\textsubscript{4}\textsuperscript{+} into zeolite. Phosphate rock can be blended with this urea zeolite fertiliser to act as a slow release phosphate fertiliser, whose release is controlled by two reactions (1) ion exchange of calcium into the zeolite, and (2) acid leaching from conversion of ammonium ions to nitrate, producing a fertiliser with slower release than super phosphate\textsuperscript{[20]}.

\[
2KZ + Ca^{2+}_{(aq)} \rightleftharpoons CaZ_2 + 2K^+_{(aq)} \quad (3)
\]

\[
2NH_4Z + Ca^{2+}_{(aq)} \rightleftharpoons CaZ_2 + 2NH_4^+_{(aq)} \quad (4)
\]

Zeolites can be loaded using K\textsuperscript{+} and NH\textsubscript{4}\textsuperscript{+} salts following the synthesis stage, or by treating a waste stream containing the desired nutrient, for example, NH\textsubscript{4}\textsuperscript{+} and PO\textsubscript{4}\textsuperscript{3-} can both be removed from solution by substituting NH\textsubscript{4}\textsuperscript{+} with Ca\textsuperscript{2+} in zeolite P which then results in the precipitation of Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}\textsuperscript{[21]}, and the spent zeolite can be used as a soil amendment.

\[\text{Figure 5: An illustration of nutrient cation exchange between zeolite fertiliser and the soil-water environment}\]
1.3 The Market for Slow Release Fertilisation

The Australian fertiliser market is summarised in Table 2 below. The fertiliser market is filled with a variety of different fertiliser types that target different applications; Table 3 below lists a few different potential zeolite controlled release fertilisers, as well as some established fertilisers for comparison. The scale of the fertiliser market in terms of zeolites is illustrated in Table 4 below.

Table 2: Australian fertiliser consumption in terms of nutrients (tonnes) [2]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (N)</td>
<td>762,000</td>
<td>811,900</td>
<td>857,300</td>
<td>1,003,000</td>
</tr>
<tr>
<td>Phosphorus (P)</td>
<td>478,800</td>
<td>436,700</td>
<td>482,100</td>
<td>432,900</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>158,900</td>
<td>203,800</td>
<td>195,600</td>
<td>192,300</td>
</tr>
<tr>
<td>Total</td>
<td>1,399,700</td>
<td>1,452,400</td>
<td>1,535,000</td>
<td>1,628,200</td>
</tr>
</tbody>
</table>

Table 3: Fertiliser prices

<table>
<thead>
<tr>
<th>Fertiliser</th>
<th>N</th>
<th>P</th>
<th>K</th>
<th>Ca</th>
<th>Cost [A] (AU/tonne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea (U) [3]</td>
<td>46</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>340</td>
</tr>
<tr>
<td>Phosphate Rock (P)</td>
<td>0</td>
<td>14</td>
<td>0</td>
<td>35</td>
<td>55 [B]</td>
</tr>
<tr>
<td>K-Zeolite (K) [C]</td>
<td>0</td>
<td>0</td>
<td>13.0</td>
<td>0</td>
<td>150</td>
</tr>
<tr>
<td>NH4-Zeolite (N) [C]</td>
<td>5.0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>150</td>
</tr>
<tr>
<td>U-K [D]</td>
<td>7.7</td>
<td>0</td>
<td>10.8</td>
<td>0</td>
<td>182</td>
</tr>
<tr>
<td>U-N [D]</td>
<td>11.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>182</td>
</tr>
<tr>
<td>U-K-P [E]</td>
<td>5.1</td>
<td>4.7</td>
<td>7.2</td>
<td>11.7</td>
<td>140</td>
</tr>
<tr>
<td>U-N-P [E]</td>
<td>7.9</td>
<td>4.7</td>
<td>0</td>
<td>11.7</td>
<td>140</td>
</tr>
<tr>
<td>CAN [3]</td>
<td>27</td>
<td>0</td>
<td>0</td>
<td>8.4</td>
<td>370</td>
</tr>
<tr>
<td>DAP [3]</td>
<td>18</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>458</td>
</tr>
<tr>
<td>NPK Extra [3]</td>
<td>7.5</td>
<td>16.4</td>
<td>10.3</td>
<td>0</td>
<td>502</td>
</tr>
<tr>
<td>Pasture Perfect [3]</td>
<td>12.6</td>
<td>0</td>
<td>19.8</td>
<td>0</td>
<td>273</td>
</tr>
<tr>
<td>Murate of Potash [3]</td>
<td>0</td>
<td>0</td>
<td>49.5</td>
<td>0</td>
<td>395</td>
</tr>
</tbody>
</table>

[A] For December 2002. [B] Australia’s phosphate rock requirements have always been predominantly imported [22] therefore the price is controlled by international commodity markets, the price for phosphate rock was $US41 in 2002 [23]. An exchange rate of $AU1 = $US0.75 is assumed. [C] Assuming a cation exchange capacity of 3.5 meq/g for Na loaded zeolite. [D] Urea is added to fill zeolites void space in dehydrated zeolite, taken to be 0.35, and the specific gravity is assumed to be 2.3 for all zeolite. [E] One part (mass) phosphorus rock is added to two parts urea filled zeolite.

<table>
<thead>
<tr>
<th>Product</th>
<th>Market Demand [A] (MT/year)</th>
<th>Zeolite Value ($AU/T)</th>
<th>Market Value (Millions $AU/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-Zeolite [A]</td>
<td>1.5</td>
<td>150</td>
<td>225</td>
</tr>
<tr>
<td>Urea-NH4-Zeolite [B]</td>
<td>7.0</td>
<td>150</td>
<td>1050</td>
</tr>
<tr>
<td>Blend [C]</td>
<td>7.5</td>
<td>150</td>
<td>1125</td>
</tr>
</tbody>
</table>

[A] Market demand for zeolite component of fertiliser product assuming that it supplies the total 1999 market requirements for potassium. [B] Market demand for zeolite component of fertiliser product assuming that it supplies the total 1999 market requirements for nitrogen. [C] Blend of U-K and U-N such that N and K markets are satisfied, occurs with (20% U-K and 80% U-N)

Based upon information given by IFA et al. (1999)[24], the total world use of nitrogen (N) and potassium (K₂O) in fertilisers for 1997, is roughly 70 Mt, and 20 Mt respectively, and represents a significant large potential export market for fly ash zeolites.

1.4 Zeolite Synthesis from Coal Fly Ash

Many authors have investigated the hydrothermal synthesis (where the zeolitisation of aluminium and silicon takes place in water at elevated temperatures) of zeolite materials from coal fly ash as the starting material, for direct hydrothermal synthesis [15; 16; 25-45], for
hydrothermal synthesis using silica extracts\textsuperscript{[32; 46-48]}, and for hydrothermal synthesis from alkali fused fly ash\textsuperscript{[32; 49-53]}. Direct hydrothermal synthesis of fly ash is where the ash in its solid particulate form, without any prior chemical transformation, is combined with other reactants and treated hydro-thermally to produce a zeolitic product which contains both zeolite and un-reacted fly ash phases, and is the synthesis method employed in this paper.

A number of different types of zeolite have been synthesised from fly ash by previous authors using direct hydrothermal conversion with sodium hydroxide:

- FAU - Faujasite\textsuperscript{[15; 34]}, Zeolite X\textsuperscript{[31; 35; 37; 40; 54]}, Zeolite Y\textsuperscript{[54]}
- LTA - Linde Type A\textsuperscript{[15; 33-35]}
- GIS - Zeolite P\textsuperscript{[16; 21; 25; 26; 31-34; 36]}, Zeolite P\textsuperscript{1}\textsuperscript{[15; 17; 27; 30; 37; 38; 40; 43-45; 47; 54]}, Gobinsite\textsuperscript{[44]}
- ANA - Analcime\textsuperscript{[15; 27; 30; 36; 43; 54]}
- CHA - Herschelite\textsuperscript{[15]}
- SOD - Sodalite\textsuperscript{[32; 54]}, Hydroxy-Sodalite\textsuperscript{[15; 16; 25; 26; 31; 36; 38; 43; 45]}, Sodalite Octahydrate\textsuperscript{[40]}
- CAN - Cancrinite\textsuperscript{[36]}, Hydroxy-Cancrinite\textsuperscript{[15; 38; 43]}
- GME - Gmelinite\textsuperscript{[27]}
- JBW - Nepheline hydrate\textsuperscript{[27; 38]}
- PHI - Phillipsite\textsuperscript{[40]}

1.4.1 Mechanism

The mechanism for zeolite synthesis from fly ash in a batch hydrothermal synthesis process has three stages; 1) The dissolution of aluminium and silicon from fly ash, 2) The deposition of aluminosilicate gel on ash surface, 3) The crystallisation of zeolite from aluminosilicate gel\textsuperscript{[25; 26]}, see Figure 6 Below.

There are three phases in fly ash from which the aluminium and silicon come from 1) Amorphous aluminosilicate glass, 2) quartz, and 3) mullite. The aluminosilicate glass phase is the largest and most unstable of these phases in the hydrothermal environment, and therefore has the highest rate of dissolution\textsuperscript{[15; 25-29]}, and is therefore the largest contributor to the zeolites produced. Quartz is less stable than mullite\textsuperscript{[15; 16; 25-27; 29; 30]}, although quartz and mullite phases are significantly more stable than the glass phase to the extent that some authors report little to no reactivity\textsuperscript{[31]} for quartz, and\textsuperscript{[32; 33]} for mullite.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{reaction_mechanism.png}
\caption{Reaction mechanism for the batch hydrothermal conversion of fly ash to zeolite}
\end{figure}
1.4.2 Factors influencing zeolitisation

There are a number of different factors which influence the zeolitisation of fly ash, they include fly ash properties, alkalinity, temperature, time, cations, templates, water, ageing and seeding. Generally but not exclusively, direct hydrothermal synthesis is carried out between 70 and 200°C, 3 and 48 hours, 0.5 and 5 mol OH\(^{-}\) per litre of solution, 2 and 20mL of solution per g of coal fly ash, and usually with Na\(^{+}\) or K\(^{+}\) cations in the form of hydroxides.

1.4.2.1 Coal Fly Ash (Aluminosilicate source)

As the source for both silicon and aluminium for zeolite synthesis, the properties of fly ash will have a significant influence on the composition and quantity of these species liberated into solution and therefore the composition of the zeolite produced.

The important components of fly ash are 1) Amorphous aluminosilicate glass, 2) Quartz, 3) Mullite, 4) Metal oxides (eg Na\(_2\)O, K\(_2\)O, CaO), 5) Iron Oxides (eg Hematite and Magnetite), 6) Unburned Carbon, and 7) Trace elements. Highest synthesis yields >80wt% correspond to highest glass containing fly ash, the lower conversions (yields) are attributed to (i) larger contents of non-reactive phases (hematite, magnetite) in fly ash, and (ii) larger content of resistant alumina-silicate phases (mullite, quartz)\(^{[15]}\).

The crystallisation of zeolites can be split into primary and secondary crystallisation stages, where the primary crystallisation is fuelled by the amorphous aluminosilicate glass, while the secondary crystallisation is fuelled by the aqueous silica excess left by primary crystallisation and further extracts from quartz and mullite\(^{[27]}\). As the largest and most reactive aluminosilicate source, the glass phase has the greatest influence over the composition and type of zeolite produced. Fly ashes with similar bulk SiO\(_2\)/Al\(_2\)O\(_3\) ratios produced different zeolites under the same conditions, this is attributed to differences in the composition of glass matrix\(^{[15; 27]}\). Generally higher temperature and higher Si/Al molar ratios favour zeolite P formation, lower Si/Al and temperature favour faujasite and zeolite A\(^{[34; 35]}\). The hydrothermal product has significantly reduced Si content relative to fly ash\(^{[36]}\), Tanaka et al. (2002) calculated that only 24% of the Si eluted from fly ash was converted to Zeolite NaP1, with the remainder remaining in the effluent\(^{[35]}\). This excess Si can be utilised by the addition of easily mobilised Al materials.

Many metal oxides are readily dissolved in hydrothermal media to produce cations in solution; the effect of charged species in solution is discussed later. Of particular interest is the effect of calcium content in fly ash material on the synthesis of zeolites, materials with a calcium content exceeding a critical level (3-5 wt% of fly ash), have a suppressing effect on the crystallisation of zeolites (in particular zeolite A)\(^{[56]}\).

The magnetite phase is not altered during the course of hydrothermal reaction\(^{[27; 30]}\). The iron oxide and unburned carbon phases, which are not altered during hydrothermal synthesis, form part of the zeolitic product; their presence in fly ash makes it impossible to produce a pure zeolite product.
Most anion forming elements are mobile and largely extracted into aqueous phase during hydrothermal synthesis\textsuperscript{[17]}, including As, Se\textsuperscript{[17]}, Mo\textsuperscript{[17; 37]}, B, and P\textsuperscript{[37]}. Cations forming heavy metals (eg Cu, Pb, Zn) remain in zeolite product (i) as precipitated hydroxides or (ii) absorbed into the zeolite framework\textsuperscript{[17]}.

1.4.2.2 Alkalinity

The OH\textsuperscript{−} ions create an environment which mobilise Si and Al oxides into solution, OH\textsuperscript{−} ions control the concentrations of saturation and supersaturation which are a key to nucleation and crystal growth\textsuperscript{[56]}. The strength of this base is related to the cations it is coupled with, NaOH has a greater efficiency for dissolving quartz and Mullite than KOH\textsuperscript{[27]}, and NaOH solutions produce greater yields of zeolite than KOH solution\textsuperscript{[15]}. The use of NH\textsubscript{4}OH as base resulted in no change in the CEC compared to fly ash starting material\textsuperscript{[37]}.

Increased pH will increase reactant concentrations in solution; this will accelerate the rate of crystallisation\textsuperscript{[56]}. Dissolution is low at low OH\textsuperscript{−} concentration, and results in low zeolite yields\textsuperscript{[25; 26]}. Increasing NaOH concentration result in increased Mullite digestion\textsuperscript{[27]}, however increasing the NaOH concentration results in a greater increase in Si dissolution than the increase in Al dissolution from fly ash\textsuperscript{[29; 33]}, resulting in a increase in the Si/Al ratio in solution which influences the gel composition and subsequently zeolite product type produced\textsuperscript{[33]}.

1.4.2.3 Temperature and time

The first phase to crystallise from solution according to Ostwald’s rule of successive phase transformation is the thermodynamically least favourable phase, with time this phase will be followed successively with increasingly more stable phases\textsuperscript{[56]}, while increasing temperature increases the nucleation and growth rate of zeolite crystals\textsuperscript{[56]}.

Increasing temperature results in increased mullite digestion\textsuperscript{[27]}, however it also results in a greater increase in Si dissolution than it increases Al dissolution from fly ash\textsuperscript{[29; 33]}, resulting in an increase in the Si/Al ratio in solution which influences the gel composition and subsequently zeolite product type produced\textsuperscript{[33]}. Generally higher temperature favour zeolite P formation, while lower temperatures favour faujasite and zeolite A\textsuperscript{[34]}.

1.4.2.4 Charged molecules and templates

Templates are structure directing species which increase the stability of particular aluminosilicate structures during zeolite synthesis depending on the properties of template (size and charge), and so have a significant influence on the structure and composition of zeolites produced\textsuperscript{[56]}. The use of sodium produces FAU, EMT, MAZ, ECR-1, and MOR framework structure types, while potassium produces LTL, ERI, and OFF framework structure types\textsuperscript{[56]}.
In addition to being structure and composition directing species, cations also influence the rate of zeolite synthesis\cite{56}. For a fixed 3 hour reaction time and fixed pH, increasing sodium concentration results in increased zeolite P yield, and an increasing potassium chabazite yield for sodium concentration less than potassium concentration, starting from no potassium chabazite when sodium concentration is zero\cite{25; 26}.

1.4.2.5 Solvent

Water acts as a template by its interaction with cations, in addition to its action as a solvating and hydrolysing agent\cite{56}. Water molecules also enhance crystal growth by filling void space which stabilises the structures\cite{56}. Increasing the liquid to solid ratio in the hydrothermal synthesis of zeolites from fly ash was found to increased dissolution of mullite, quartz and glassy matrix\cite{15}, increase yield\cite{15; 30}, and decrease reaction rate\cite{15; 28; 30}.

2 MATERIALS AND METHODS

In this work, the direct hydrothermal synthesis method was employed to produce a zeolitic product from fly ash, which contains both zeolite and un-reacted fly ash phases using batch hydrothermal reactors. Fly ash and all hydrothermal products were analysed using x-ray diffraction (XRD). The fly ash and a selection of hydrothermal products were characterised using elemental analysis, and scanning electron microscopy (SEM).

2.1 Synthesis

The reactors were heated in a convective oven, two at a time, placed with geometric symmetry perpendicular to hot air flow. Reaction temperatures were monitored using a thermocouple attached to reactor surface. The oven is programmed such that the reactors reach reaction temperature over a 2 hour period, as illustrated in Figure 7 below. On completion of reaction period, reactors cool convectively in ambient conditions until surface temperature ~70°C (~50 min), at which point they are opened and the contents vacuum filtered hot, and washed with double distilled water.

![Temperature vs Time Graph](image)

- $T_1 = \text{Oven temperature set point (ramp)}$
- $T_2 = \text{Oven temperature set point (reaction)}$
- $T_3 = \text{Reactor surface temperature (reaction)}$
- $t_1 = \text{Ramp time}$
- $t_2 = \text{Reaction time}$
- $t_3 = \text{Cooling time}$

Figure 7: Heating profile for batch hydrothermal synthesis experiments
There are a number of different reaction conditions important to the direct hydrothermal synthesis of zeolite from fly ash, including:

- Reaction Temperature
- Reaction Time
- \( n \) (Si/Al ratio, related to fly ash composition)
- \( M \) (Cation type)
- \( pH \) (related to \( x \) and \( p \))
- \( p \) (H\(_2\)O/Al ratio)
- \( m \) (excess \( M^+ \)/Al ratio)

The terms in bold are defined by the reaction mixture equation, Equation 5, which is based on 1 mole of Al.

\[
\frac{1+m}{z} M^{z+} (OH_x^- + (NO_3^-)_{1-x})_z 0.5Al_{2}O_{3} nSiO_{2} \cdot pH_{2}O
\]  

Nitrate was chosen as the anion to accompany Na\(^+\) in the experiments to differentiate Na\(^+\) from OH\(^-\) in NaOH, over more traditional anions (Cl\(^-\), CO\(_3^{2-}\)) because:

- It has highest solubility which increases with temperature
- It has a neutral pH
- Cl\(^-\) has low solubility which decreases with increasing temperature
- CO\(_3^{2-}\) is divalent with NaCO\(_3^-\) a weak base therefore not independent of pH, and will have a pH buffering effect, see Equation 6 below

\[
H_2O + NaCO_3^- \rightleftharpoons OH^- + Na^+ + HCO_3^-
\]  

Due to the expressed condition of the sponsor for this work, that all information pertaining to specific reaction conditions is withheld, and therefore the reaction conditions used are not given in this paper.

### 2.2 Quantitative X-ray diffraction

X-ray powder diffraction patterns are produced from the diffraction of x-rays by the different crystal planes within the mineral. Different minerals have different unit cell (smallest divisible unit of crystal structure which is repeated to make the whole mineral) structure, and therefore diffract differently. The pattern that is produced is unique to the mineral from which it was produced (a mineralogical fingerprint). Therefore this technique allows for the qualitative identification of the phases present in a sample.

The peak intensities of a phase in XRD are related to the volume fraction of that phase in the sample. The value of peak intensities can be used as a semi-quantitative measurement. Two major limitations with this technique are:

- Uncertainty relating to particle counting statistics
- Intensity attenuation/adsorption differences between samples
By adding an internal standard (e.g., corundum), the peak intensity of each phase relative to corundum (I/Ic, reference intensity ratio) can be determined, overcoming the second problem above. This technique is considered to be quantitative as composition of phase in sample can be calculated; however, the error can be significant.

These techniques are not suitable where excessive peak overlap occurs, or where quantitative information on trace phases is required.

The diffraction pattern of any known mineral phase can be modelled from theory (using unit cell and atomic position information), by using full profile Rietveld analysis, which fits model to experimental data (for all peaks over whole experimental 2θ range) by refining instrument, microstructural, and atomic parameters, allowing the quantitative determination of the mineralogical phases present in the material (including trace phases) with significantly improved error relative to other techniques.

The Rietveld method was chosen for this work because:
- Quantitative information for trace phases was desired
- Significant (sometimes total) peak overlap is present in samples
- Best confidence in the reliability of result is desired

For XRD experiments, solid samples were ground to finely divided form and standardised samples prepared by combining a measured quantity of sample with a measured quantity of corundum with thorough mixing. The analysis was conducted on a Siemens D500 diffractometer using Cu kα wavelength, with 1° divergence slits, over the range 3 – 70° 2θ, with a 0.02° step size, and a speed of 0.6° min⁻¹. The resulting diffractograms* were quantitatively analysed using multi-component Rietveld refinement method** with the program Rietica*** over the 2θ range 15 – 70°, because at 2θ below 15°, the beam footprint exceeds the bounds of the sample holder resulting in reduced incident intensity to the sample, and therefore peak intensity from the sample.

Mineral phases used in quantitative analysis include Corundum† (ICSD #73725), Quartz‡ (ICSD #200722), Mullite|$^*$ (ICSD #100805), Hercynite§ (ICSD #86576), Magnetite¶ (ICSD #82237), Hematite|| (ICSD #82135), Analcime** (ICSD #87555), Cancrinite*** (ICSD #63719), Chabazite†† (ICSD #18197), Zeolite NaP1‡‡ (ICSD #9950), Gmelinite‡§ (ICSD #31240), and Sodalite‡¶ (ICSD #56710).

---

* Due to unsatisfactory capacity of Rietica to model the amorphous backgrounds present in samples, the backgrounds were fit and removed separately using manual peak removal and background modelling in a spreadsheet.
† Inorganic Crystal Structure Database (ICSD)
‡ Na1 and H2O site occupancies refined
§ Atomic positions were refined, and Ca atom occupying 12i site was replaced with a Na atom occupying 6h site
** Atomic positions for Na were refined, and a H2O molecule was added to occupy 8e site
2.3 Elemental Analysis
Elemental analysis was conducted on fly ash and selected hydrothermal products, HTP1 to HTP4, using inductively coupled plasma mass spectrometry (ICP-MS), and atomic emission spectroscopy (AES).

2.4 SEM
For SEM analysis, solid fly ash and HTP1 samples were set into an epoxy resin and polished to give a smooth cross section of particles for analysis. SEM analysis included the use of EDS* and EMPA† point analysis for the determination of local chemical composition.

3 RESULTS AND DISCUSSION

3.1 Morphology and Composition
To evaluate the chemical and mineral variation within and between fly ash particles, SEM was used in conjunction with EPMA analysis, with the mineralogy inferred from the chemistry. A selection of sample points from a range of particle types is illustrated in Figure 8 below for fly ash, with the chemistry of test points given in Table 5.

![Figure 8: SEM images of fly ash cross sections illustrating the location of EPMA point analysis](image)

---

* Philips XL30 SEM with Oxford Instruments EDS (SiLi detector with super ultra thin window) using INCA Suit version 4.00 software
† JEOL JXA-8600 Superprobe with data interpreted by JEOL XM-86PAC quantitative analysis program
It can be seen that there is significant chemical and mineralogical variation between different ash particles and even within a single particle. From Table 7 we know that the iron content is high, and the content of iron in mineral phases is low (see Table 8 below), therefore significant iron must be present in the glass phase, this is supported by the EPMA analysis presented in Table 5, where all the glass phases tested contained at least 4% iron.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Point</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>Tot</th>
</tr>
</thead>
<tbody>
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<td>A</td>
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<td>37.9</td>
<td>4.27</td>
<td>0.59</td>
<td>0.74</td>
<td>1.97</td>
<td>1.18</td>
<td>0.61</td>
<td>102.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>59.0</td>
<td>36.3</td>
<td>4.06</td>
<td>0.64</td>
<td>1.37</td>
<td>0.95</td>
<td>103.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>60.4</td>
<td>25.9</td>
<td>5.37</td>
<td>0.93</td>
<td>2.23</td>
<td>1.77</td>
<td>97.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
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<td>35.2</td>
<td>6.64</td>
<td>0.52</td>
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<td>0.86</td>
<td>0.98</td>
<td>100.9</td>
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<td>E</td>
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<td>13.0</td>
<td>2.09</td>
<td>1.84</td>
<td>0.76</td>
<td>1.44</td>
<td>1.5</td>
<td>101.0</td>
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<td>6.77</td>
<td>0.65</td>
<td>0.65</td>
<td>1.37</td>
<td>0.57</td>
<td>1.85</td>
<td>93.0</td>
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</tr>
<tr>
<td>G</td>
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<td>35.8</td>
<td>4.17</td>
<td>1.96</td>
<td>0.77</td>
<td>1.68</td>
<td>102.8</td>
<td></td>
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<td>H</td>
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<td>9.11</td>
<td>0.65</td>
<td>0.83</td>
<td>1.07</td>
<td>1.75</td>
<td>0.59</td>
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<tr>
<td>I</td>
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<td>40.6</td>
<td>7.06</td>
<td>0.51</td>
<td></td>
<td></td>
<td>101.8</td>
<td></td>
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<tr>
<td>J</td>
<td>38.5</td>
<td>31.1</td>
<td>21.1</td>
<td>3.37</td>
<td>1.76</td>
<td></td>
<td>0.87</td>
<td>1.90</td>
<td>99.5</td>
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<td>K</td>
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<td>4.38</td>
<td>0.58</td>
<td>0.52</td>
<td>1.84</td>
<td>0.98</td>
<td>0.87</td>
<td>102.8</td>
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<td>Glass</td>
<td>Average</td>
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<td>34.6</td>
<td>7.81</td>
<td>2.04</td>
<td>0.98</td>
<td>1.46</td>
<td>1.21</td>
<td>1.19</td>
<td>100.6</td>
<td></td>
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<tr>
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<td>Std Dev</td>
<td>6.5</td>
<td>3.8</td>
<td>5.16</td>
<td>1.36</td>
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<td>0.11</td>
<td>0.43</td>
<td>0.56</td>
<td>3.0</td>
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</tr>
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<td>19.3</td>
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<td>15.4</td>
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<td>100.4</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>M</td>
<td>69.0</td>
<td>19.4</td>
<td></td>
<td>9.52</td>
<td></td>
<td>99.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hematite</td>
<td>N</td>
<td>0.93</td>
<td>0.59</td>
<td>91.5</td>
<td></td>
<td></td>
<td>93.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hercynite</td>
<td>O</td>
<td>8.30</td>
<td>29.5</td>
<td>52.82</td>
<td>3.98</td>
<td>3.18</td>
<td>1.50</td>
<td>5.19</td>
<td>105.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unknown</td>
<td>P</td>
<td>24.8</td>
<td>29.0</td>
<td>16.0</td>
<td>9.09</td>
<td>4.22</td>
<td>5.39</td>
<td>1.81</td>
<td>91.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Q</td>
<td>15.7</td>
<td>39.0</td>
<td>24.1</td>
<td>5.25</td>
<td>6.92</td>
<td>4.22</td>
<td>2.58</td>
<td>98.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>R</td>
<td>24.3</td>
<td>28.6</td>
<td>26.3</td>
<td>7.52</td>
<td>3.08</td>
<td>0.96</td>
<td>1.41</td>
<td>92.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[A] Mineralogy inferred from chemistry [B] The electron beam volume of excitation of glass phase may include mullite phases which grow within the glass phase, giving a composition which is a blend of glass and mullite phases.

By comparison of fly ash starting material and a hydrothermal product HTP1 produced using batch non-agitated hydrothermal reaction, and characterised using SEM, several transformations are evident (see Figures 9 and 10):

- The small particles which dominate fly ash are not present in hydrothermal products, the average particle size has significantly increased, often the product is a single solid plug at the bottom of reactor, which is crushed into granules for handling and analysis.
- Three types of particle morphology exist in the hydrothermal product:
  1. Macro-particles which includes components of un-reacted fly ash particles glued together by or encapsulated within zeolite phases (see Figures 9(i) and 9(ii))
  2. Single phase product particles which contain few included un-reacted fly ash particles, and have highly geometric crystalline structure (see particles A and B in Figures 9(iii) and (iv))

*Note Figure 9(iv) is an image of a coarsely polished cross section which fractures crystals along crystal planes.*
3) Excluded components of non-reacted fly ash particles (see Figures 9(i) and 10(ii))

- From inspection of the light contrast phases (high atomic number, e.g., high iron), two types are present:
  1) Phases which retain full spherical form (un-reacted fly ash particles, see particles C in Figure 9(iii))
  2) Free iron phases which often occur in spherical-like clusters indicating originally part of spherical fly ash particle where more reactive phases have etched away (see Figure 10(iv))
- Quartz particles show significant signs of internal etching (see Figures 10(i) and (ii))
- Ghosts of fly ash particles remain where glass has been completely etched away to reveal mullite crystals which retain the overall morphology of original fly ash particle (see Figure 10(iii)). This demonstrates that mullite was accessible to solution but did not dissolve under the reaction conditions of HTP1

Figure 9: Particle cross sections viewed by SEM for HTP1 illustrating different zeolite phases present in hydrothermal product
All of the hydrothermal experiments presented were conducted using the non-agitated batch hydrothermal process, which was expected to follow the reaction mechanism illustrated in Figure 6. Figures 9 and 10 confirm this in part, however the zeolite phase has not grown to surround ash particles, encapsulating them and isolating them from dissolution, instead they have grown into the spaces between particles, and joined ash particles (present in close proximity to each other as sediment at the bottom of the non-agitated reactor) together like a glue (see Figure 9(ii)). The difference is likely to be due to the absence of viscous effects in non-agitated systems which are present in agitated systems.

This type of growth creates a spongy macro-scale particulate product which allows access for the continued dissolution of fly ash particles with time. A consequence of large (mm scale) product particles with spongy structure is that reactant solution containing NaOH and NaNO₃ can be isolated from the wash procedure, and be present in the product. The presence of NaOH and NaNO₃ in products is supported by their bulk Na₂O contents, see Table 7, which are larger than prescribed by the zeolite phases present, see Table 8. However neither NaOH nor NaNO₃ were detected in any XRD patterns. The discrepancy is most likely due to the formation of amorphous alumino-silicate gel, illustrated in Figure 6, which has not crystallised to form any zeolite. Either way additional x-ray amorphous phases contribute to the “other” components in Table 8. Under these circumstances the dissolution of amorphous glass phases in fly ash cannot be investigated directly using quantitative XRD results.
The macro product particles are too complicated to discriminate between the different zeolite phases and hydro-gel, therefore EDS analysis of zeolites was limited to the highly geometric crystalline phases which are clearly identifiable.

From fly ash characterisation we know that a significant portion of iron is present in the glass phase of fly ash. However this has not prevented it from being dissolved by the alkaline hydrothermal solution. The iron released by glass dissolution has been incorporated into the zeolite phases produced by hydrothermal reaction (see Table 6), although it is unknown how it is incorporated (within framework, as a charge balancing cation, or discreet nano-particles).

Although the fly ash has significant chemical and mineralogical variation, the variation in the composition of zeolite particles (A and B) illustrated in Figure 9(iii) is low, see Table 6.

<table>
<thead>
<tr>
<th>Phase</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>H₂O</th>
<th>Tot</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>56.3</td>
<td>18.4</td>
<td>5.09</td>
<td>0.15</td>
<td>0.03</td>
<td>12.1</td>
<td>0.09</td>
<td>0.11</td>
<td>0.11</td>
<td>8.11</td>
<td>100.6</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>1.6</td>
<td>0.6</td>
<td>0.50</td>
<td>0.26</td>
<td>0.09</td>
<td>0.7</td>
<td>0.08</td>
<td>0.07</td>
<td>0.17</td>
<td>1.04</td>
<td>2.9</td>
</tr>
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<td>B</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>56.3</td>
<td>22.6</td>
<td>2.29</td>
<td>0.48</td>
<td>0.00</td>
<td>10.2</td>
<td>2.14</td>
<td>0.56</td>
<td>0.05</td>
<td>5.17</td>
<td>99.9</td>
</tr>
<tr>
<td>Standard Deviation</td>
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<td>1.1</td>
<td>0.42</td>
<td>0.17</td>
<td>0.01</td>
<td>1.9</td>
<td>1.40</td>
<td>0.13</td>
<td>0.05</td>
<td>1.19</td>
<td>3.2</td>
</tr>
</tbody>
</table>

(A) Compositions based on 14 analysis points for phase A, and 10 for phase B

During the hydrothermal process some elements from the fly ash are leached and not present in solid product, while others present in aqueous reactants form part of the solid product (eg. Na, H₂O). Iron has a very low solubility under hydrothermal reaction conditions, therefore all iron inputted from the fly ash is expected to be present in the hydrothermal product. If Fe₂O₃ is used as a tracer, changes in the total Al and Si content and in the quartz, mullite and zeolite contents can be quantified.

By using Fe₂O₃ as a tracer (see Table 9), we see that there is a general reduction in the SiO₂ content of hydrothermal products from that in the fly ash, while the Al₂O₃ content remains roughly the same. For HTP1, HTP2, and HTP4, the source of Al in zeolite is almost completely from the glass phase, and yields are 0.45, 0.19, and 0.12 grams of zeolite per gram of fly ash reactant respectively.
Table 7: Bulk chemical analysis of fly ash and a selection of hydrothermal products (wt%)

<table>
<thead>
<tr>
<th>Component</th>
<th>Fly Ash&lt;sup&gt;[A]&lt;/sup&gt;</th>
<th>Fly Ash</th>
<th>HTP1</th>
<th>HTP2</th>
<th>HTP3</th>
<th>HTP4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>53.7</td>
<td>54.8</td>
<td>38.3</td>
<td>39.4</td>
<td>32.7</td>
<td>42.8</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>23.7</td>
<td>21.9</td>
<td>23.1</td>
<td>23.4</td>
<td>21.9</td>
<td>19.3</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>14.5</td>
<td>14.6</td>
<td>14.3</td>
<td>14.6</td>
<td>13.7</td>
<td>13.4</td>
</tr>
<tr>
<td>CaO</td>
<td>1.7</td>
<td>1.78</td>
<td>1.80</td>
<td>1.80</td>
<td>1.72</td>
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<td>MgO</td>
<td>1.1</td>
<td>1.11</td>
<td>1.16</td>
<td>1.18</td>
<td>1.11</td>
<td>0.98</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.27</td>
<td>0.30</td>
<td>6.93</td>
<td>9.57</td>
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<td>7.47</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.94</td>
<td>0.95</td>
<td>0.46</td>
<td>0.29</td>
<td>0.05</td>
<td>0.61</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1.4</td>
<td>1.42</td>
<td>1.42</td>
<td>1.43</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>Mn&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.14</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.12</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>1.7</td>
<td>1.62</td>
<td>0.57</td>
<td>0.94</td>
<td>0.09</td>
<td>1.05</td>
</tr>
<tr>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.09</td>
<td>0.22</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.10</td>
</tr>
<tr>
<td>SrO</td>
<td>0.34</td>
<td>0.31</td>
<td>0.33</td>
<td>0.33</td>
<td>0.31</td>
<td>0.29</td>
</tr>
<tr>
<td>BaO</td>
<td>0.48</td>
<td>0.41</td>
<td>0.44</td>
<td>0.45</td>
<td>0.41</td>
<td>0.38</td>
</tr>
<tr>
<td>Total</td>
<td>100.1</td>
<td>99.5</td>
<td>88.9</td>
<td>93.5</td>
<td>89.7</td>
<td>89.3</td>
</tr>
</tbody>
</table>

<sup>[A]</sup> From XRF

Table 8: Bulk mineral analysis of fly ash and a selection of hydrothermal products (wt%)

<table>
<thead>
<tr>
<th>Component</th>
<th>Fly Ash</th>
<th>HTP1</th>
<th>HTP2</th>
<th>HTP3</th>
<th>HTP4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>13.8</td>
<td>3.8</td>
<td>5.7</td>
<td>1.4</td>
<td>8.2</td>
</tr>
<tr>
<td>Mullite</td>
<td>11.0</td>
<td>13</td>
<td>11</td>
<td>4.0</td>
<td>9.2</td>
</tr>
<tr>
<td>Hercynite</td>
<td>4.6</td>
<td>4.1</td>
<td>4.8</td>
<td>4.7</td>
<td>6.3</td>
</tr>
<tr>
<td>Magnetite</td>
<td>1.3</td>
<td>2.1</td>
<td>1.5</td>
<td>1.8</td>
<td>?</td>
</tr>
<tr>
<td>Hematite</td>
<td>0.9</td>
<td>?</td>
<td>0.7</td>
<td>0.7</td>
<td>?</td>
</tr>
<tr>
<td>Analcime</td>
<td>1.4</td>
<td></td>
<td>6.1</td>
<td>42</td>
<td>1.9</td>
</tr>
<tr>
<td>Cancrinite</td>
<td></td>
<td>39</td>
<td>5.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chabazite</td>
<td>3.3</td>
<td></td>
<td></td>
<td>8.5</td>
<td>1.9</td>
</tr>
<tr>
<td>Gmelinite</td>
<td></td>
<td></td>
<td></td>
<td>13</td>
<td>1.0</td>
</tr>
<tr>
<td>Zeolite NaP1</td>
<td>68.4</td>
<td>33</td>
<td>57</td>
<td>37</td>
<td>66</td>
</tr>
<tr>
<td>Other&lt;sup&gt;[A]&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>[A]</sup> x-ray amorphous phases and mineral phases not quantified (indicated by ?) due to 8 phase limitation of Rietica and excessive peak overlap of trace iron phase peaks with major zeolite phases

Table 9: Ratio of components composition (wt%) to that of Fe<sub>2</sub>O<sub>3</sub> Tracer (wt%)<sup>[A]</sup>

<table>
<thead>
<tr>
<th>Component</th>
<th>Fly Ash</th>
<th>HTP1</th>
<th>HTP2</th>
<th>HTP3</th>
<th>HTP4</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.70</td>
<td>2.68</td>
<td>2.70</td>
<td>2.38</td>
<td>3.20</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.63</td>
<td>1.61</td>
<td>1.61</td>
<td>1.60</td>
<td>1.44</td>
</tr>
<tr>
<td>Quartz</td>
<td>1.95</td>
<td>0.26</td>
<td>0.39</td>
<td>0.10</td>
<td>0.62</td>
</tr>
<tr>
<td>Mullite</td>
<td>0.76</td>
<td>0.90</td>
<td>0.78</td>
<td>0.29</td>
<td>0.69</td>
</tr>
<tr>
<td>Zeolites</td>
<td>---</td>
<td>3.07</td>
<td>1.33</td>
<td>3.66</td>
<td>0.80</td>
</tr>
</tbody>
</table>

<sup>[A]</sup> Multiplying this ratio by grams of Fe<sub>2</sub>O<sub>3</sub> per gram of fly ash (0.145) gives the yield in grams of component per gram of fly ash reactant

From analysis of trace element concentrations in fly ash and hydrothermal products following various hydrothermal conditions (see Table 10 below), showed some elements were significantly reduced in concentration (As and Mo), some were slightly reduced (Hg, Pb, Cu, V), some stayed constant (Cr, Ni, Zn), and some were already at or below the detection limit of analysis (B, Cd, Se). Most of the elements of greatest concern have been reduced in concentration to or below their average levels in soil, shale, or crust, and not likely to present a problem for agricultural application.
Table 10: Trace element analysis for fly ash and a selection of hydrothermal products (ppm)

<table>
<thead>
<tr>
<th>Element</th>
<th>Soil (ppm)</th>
<th>Shale (ppm)</th>
<th>Crust (ppm)</th>
<th>Fly Ash</th>
<th>HTP1</th>
<th>HTP2</th>
<th>HTP3</th>
<th>HTP4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>As 7</td>
<td>13</td>
<td>1</td>
<td>6</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>1</td>
</tr>
<tr>
<td>Boron</td>
<td>B 30</td>
<td>130</td>
<td>10</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd 0.6</td>
<td>0.3</td>
<td>0.2</td>
<td>0.5</td>
<td>0.5</td>
<td>&lt;0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg 0.1</td>
<td>0.18</td>
<td>0.08</td>
<td>0.07</td>
<td>0.09</td>
<td>0.05</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Mo 1</td>
<td>2.6</td>
<td>1.5</td>
<td>12.5</td>
<td>2</td>
<td>2.5</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb 20</td>
<td>25</td>
<td>13</td>
<td>52</td>
<td>41</td>
<td>49</td>
<td>30</td>
<td>38</td>
</tr>
<tr>
<td>Selenium</td>
<td>Se 0.4</td>
<td>0.5</td>
<td>0.05</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

Elements of greatest concern

3.2 Alkalinity (pH)

A number of zeolite products were produced from fly ash using non-agitated batch reactor over a range of pH conditions. The diffraction pattern for fly ash A and three of these products is presented in Figure 11, from which the following observations can be noted:

- The emergence of zeolite peaks
- Increasing zeolite peak intensity with increasing reaction soup pH
- A shift in zeolites produced from sodalite to cancrinite with increasing pH
- A decrease in the quartz peak with increasing pH

However there are limitations with direct peak comparison due to peak overlap between sodalite and cancrinite products. There are 4 major peaks which emerge (see Figure 11) at 2θ of 13.9, 18.8, 24.2 and 27.4. The first and third of these peaks corresponds to the 011 and 112 hkl orientations of sodalite, while all four peaks correspond to the 110 011 030 121 hkl orientations of cancrinite respectively. Rietveld refinement is needed to de-convolute these peaks. From the quantitative results (see Figures 12 and 13) we see:

- The consumption of quartz and mullite with increasing reactant pH
- The emergence of zeolite phases cancrinite and sodalite and their relative abundance as a function of pH
Figure 11: XRD patterns of fly ash A and hydrothermal products of fixed m and increasing pH, as well as individual sodalite and cancrinite zeolite phases.

Figure 12: Mineral compositional trends for hydrothermal products as a function of reaction pH (i) m = constant, (ii) X = 1

Figure 13: Component composition expressed as a fraction of original component composition in fly ash (wt% / wt%)

* Note: If fraction > 1 then the component is present in a greater concentration in hydrothermal product than in fly ash reactant. For example, between first two pH conditions where glass is dissolving
From Figure 12(i), where m is fixed and pH is varied, the yield and type of zeolite produced by hydrothermal reaction changes. By comparison, from Figure 12(ii), the same pH conditions are investigated with x = 1 therefore different m. The abundances and types of zeolite produced are different to the fixed m conditions. Clearly M⁺ and OH⁻ play a different role in the overall reaction mechanism.

Previously Murayama, et al. (2002)[25; 26] investigated the substitution of NaOH and KOH for Na₂CO₃ while maintaining a constant concentration of M in solution, and concluded that:

- The OH⁻ in alkali solution contributes to the dissolution of coal fly ash, while
- The Na⁺ contributes to the crystallisation of zeolite P

Building on this, it is proposed that:

1. OH⁻ controls the dissolution rates of Al and Si sources while
2. M⁺ controls the type of zeolite product, and the rate of zeolite crystallisation from the amorphous alumina-silicate gel
3. Together MOH and MNO₃ occupy soluble space, and the selection of different compounds and concentrations will change the saturation curves (solubility) of species that participate in the hydrothermal reaction, therefore the reaction chemistry.

When m is a constant and pH is varied, there is a general increase in the dissolution of quartz and mullite with increased pH, which supports point 1 above.

Under constant pH conditions, if m is varied, different types and quantities of zeolite are produced, which supports point 2 above.

Under condition x = 1 and pH ≥ HTP2, the fraction of original component composition for iron and x-ray amorphous phases remains close to 1 while mullite which is encapsulated within glass phase is significantly consumed, indicating the significant presence of an amorphous alumina-silicate gel. The composition of amorphous phase under condition m = constant and pH ≥ HTP2 is substantially lower than under condition x = 1, which is maintained as x approaches 1 for m = constant (solubility differences narrow), indicating that increasing m increases the rate of zeolite formation out of the amorphous alumina-silica gel precursor, which supports point 2 above.

Under condition x = 1, substantial quartz dissolution starts at a lower pH than substantial mullite dissolution occurs. Under condition m = constant, this quartz and mullite dissolution is shifted up to a higher pH. The presence of increased NaNO₃ has decreased the solubility and therefore dissolution of quartz and mullite, which supports point 3 above.

significant faster than quartz or mullite and no zeolites are forming, products have glass and mullite composition fractions > 1
3.3 Reaction time

Results from a study of reaction time on hydrothermal synthesis for conditions of constant pH, p, m and T are presented in Figure 14 below. Following an initial short reaction time, chabazite is the only zeolite product. Increased reaction time sees the emergence of new zeolite phases (Gmelinite, Analcime, and Zeolite NaP1), which agrees with Ostwald’s rule of successive phase transformation or changing solution chemistry with time. Increased time sees the continued dissolution of quartz phase towards an asymptotic limit (probably due to decreasing pH with increased zeolite production as OH− is consumed).

![Figure 14: Mineral compositional trends for hydrothermal products as a function of time (i) Wt%, (ii) Component composition expressed as a fraction of original component composition in fly ash (wt%/wt%)](image)

3.4 Water Content (p)

Under the hydrothermal conditions of constant pH and x = 1, the concentration of NaOH in initial reaction solution is constant for all p. The concentration of quartz and mullite reactants in products increases with decreasing p, while the concentration of zeolites decreases (see Figure 15). This is due to increased fly ash reactant, with decreased p, that requires dissolution, and does not have sufficient time to dissolve and react.

The concentration of zeolite product at HTP4 is 11% while it is 32% for the highest p presented, however HTP4 contained 4 times as much fly ash reactant. The total zeolite yield has increased; this is likely to be due to the presence of 4 times as much of the more reactive reactants in HTP4.

The condition HTP4 sees the emergence of Zeolite NaP1 and chabazite not produced at the higher p’s (see Figure 15). This is likely to be due to either or both:

1. The formation of zeolite and its precursor gel strips Na+ from solution, therefore available m decreases with time, and lower m favours the formation of different zeolites as discussed in Section 3.2
2. With decreasing p, the fly ash particles dissolving and contributing to the synthesis of zeolite shifts towards the more reactive particles. As a consequence the solution Si/Al ratio may also change
3.5 Cation Exchange Selectivity

The sole source of potassium in HTP1 hydrothermal reaction is from the fly ash. The total mole ratio of sodium to potassium in HTP1 reaction soup was 59. The Na/K mole ratio in phase A and B indicated in Figure 9 and Table 6 previously is 204 and 7 respectively. Clearly there is a difference in cation selectivity between these different zeolite phases, with phase A selective toward sodium (Na > K), and phase B selective toward potassium (K > Na). From this result, if both phases were loaded with potassium (for use as a fertiliser), phase A is expected to release potassium to maintain a higher soil solution concentration of potassium than phase B. In other words they will perform differently as a fertiliser; therefore different zeolite fertiliser products can be designed and produced to meet the requirements of specific applications.

3.6 Economic Implications

To give a basic idea of the economic implications of processing conditions some crude economic calculations are presented below based on reasonable assumptions.

Assuming a 300 kilo-tonne per annum zeolite plant, which sells product for $AU150 per tonne of zeolite, has an operating cost of $AU100 per tonne, operates under a 30% corporate tax rate, with a 10 year double declining depreciation period, a 15 year project life span, and a 10% discount rate. For a present value ratio of 1, the fixed capital investment is $AU100 million.

With a maximum reactor size of 30m$^3$ \cite{72}, and assuming that 80% of this volume is available for solid and liquid reactants, 300 days of 24 hours continuous operation (continuous reactors), assuming that solids (fly ash, zeolite and sodium hydroxide) have a specific gravity of 2. With an appropriate pH, an x of 1 (see Equation 5), and an aluminium (Al$_2$O$_3$) composition equal to 25wt% of fly ash, where 1 tonne of zeolite is produced per tonne of fly ash. Then 20 reactors are required per hour of residence time per 100 units of $p$.

The 30m$^3$ reactor cost $US60,000 in 1987\cite{72}. Using a ChE index of 324 in 1987\cite{73}, and an extrapolated (from ChE\cite{74}) index of 404 for 2005, a location factor of 1.3 for Australia\cite{72}, an exchange rate of $US0.75 per $AU. Assuming a plant cost factor of 4,
and that the reactor section of whole plant cannot exceed 10% of FCI, there is a 19
reactor limit. For a 3 hour residence time, p is limited to 32 which is equivalent to 11.3 g
H₂O per g Al₂O₃ in fly ash.

4 SUMMARY AND CONCLUSIONS
Zeolite synthesised from fly ash for agricultural application as a controlled release
fertiliser is a technology which offers considerable advantages as a fly ash utilisation
strategy, in terms of economic, technical and environmental performance because:

- It is a value added product capable of overcoming the transport cost barrier
  inhibiting many traditional fly ash utilisation strategies, and capable of making
  use of a substantial portion of the fly ash produced annually in Australia
- It has improved fertiliser efficiency compared to traditional fertilisers resulting in
  increased productivity, and reduced nutrients being leached into the environment

From experimental results discussed, the following conclusions can be drawn

- The presence of iron in the glass phase of fly ash has not inhibited its dissolution
- The dissolution of iron containing glass has resulted in iron containing zeolites
- The zeolite phases produced are more homogeneous in composition than the fly
  ash used to make them
- Different types of zeolite can be produced from fly ash by changing reaction
  conditions
- Different zeolite phases have different cation exchange selectivity’s therefore will
  perform differently as a controlled release fertiliser

Established experimental qualitative results have been repeated using quantitative XRD
technique including:

- The higher reactivity of quartz with OH⁻ than mullite
- Dissolution increases with increasing pH

The advantage of using XRD is that it can quantify changes in the composition of quartz
and mullite reactants, and zeolite products with changes in hydrothermal reaction
conditions, revealing more information and allowing direct comparisons of the changes
taking place with changing conditions.

- Quantitative mineral analysis revealed that the amorphous alumina-silica gel
  precursor to zeolite synthesis described in Murayama’s mechanism (see Figure
  6) does not completely crystallise to form zeolites, and is present in hydrothermal
  products.
- By using NaNO₃ the influence of m (excess M⁺), can be studied independent of
  pH (OH⁻ concentration).
- In addition to controlling the type of zeolite produced, m controls the rate of
  zeolite crystallisation from the amorphous alumina-silicate gel.
- Increasing m at constant pH reduces the solubility of reactants.
- By using Fe₂O₃ as a tracer, total yields of zeolite and total quantities of quartz
  and mullite leached per gram of fly ash reactant can be determined.
Fly ash zeolitic materials have a reduced overall impurity load as a result of leaching during the synthesis stage resulting in (1) a more environmentally friendly product, and therefore (2) a more attractive product for use in agriculture relative to fly ash.

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6 REFERENCES


