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Simulation of Synthetic Zeolites-4A and 5A Manufacturing for Green Processing

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***Abstract*— Greening the manufacture of zeolites catalysts, while simultaneously lowering production cost and is a pervasive challenge. This paper discusses the modeling and simulation of zeolites for the purpose of assessing green technology applications. The study focuses on the manufacture of zeolites 4A and 5A by the hydrogel and the kaolin conversion processes, respectively. Simulation packages were developed to characterize technical performance and do some basic economic calculations. Modifications to the flow sheet of both processes were suggested to enhance green processing. The simulation models developed were used to evaluate element utilization efficiencies, and implement heat integration for energy efficiency. Preliminary costing was also done to show that green processing can result in improved environmental performance and economics of the manufacturing processes.**

Keywords-component; Zeolites manufacture, Zeolites synthesis, Zeolite 4A, zeolite 5A, hydrogel process, Kaolin conversion process, Process Simulation, Element Utilization Efficiency.

Introduction

Zeolites are porous hydrated aluminosilicates, formed under hydrothermal conditions and were first recognized as a new type of mineral in 1756. Most commercial zeolites are high purity synthetic products made from inorganic materials. Because of their porous structure, zeolites can selectively absorb or reject molecules based on difference in shape and other properties. These characteristics have resulted in variety of uses of zeolites, especially for protecting ecosystems. These include water softening in detergents (replacing undesirable polyphosphates), absorbents for oil in industrial spills, gas separation, water filtration and heavy metal removal in water purification and wastewater treatment. Zeolite catalysts play an important role in the overall profitability of these applications. Minimizing the zeolites production costs while simultaneously greening the process and minimizing the zeolites production cost is a challenge to zeolites producers. Developing validated simulation models of the zeolites production processes would provide the manufacturer with an excellent tool to address these challenges.

Currently there are some 40 different natural zeolites and roughly 150 synthetic zeolites, including zeolites A. The pore diameter of zeolites type A is between 3 Å (angstrom) and 10 Å (1 nm). The pore diameter of zeolite 4A is 0.36-0.40 nm (around 4 Å), and for zeolite 5A it is 0.42 – 0.44 nm (around 5 Å). Typical chemical compositions of zeolite 4A gel and dry Zeolite 4A [1, 2] are

($2Na_2O$-Al_2O_3-$1.75SiO_2$-$70H_2O$) Zeolite 4A Gel
($2Na_2O$-Al_2O_3-$1.75SiO_2$-$6H_2O$) Zeolite 4A dry (25 wt% H_2O)

Typical chemical compositions of wet and dry Zeolite 5A are:
($0.7CaO$-$0.3Na_2O$-Al_2O_3-$2SiO_2$-$70H_2O$) (Wet)
($0.7CaO$-$0.3Na_2O$-Al_2O_3-$2SiO_2$-$4.5H_2O$) (25 wt% water)

I. Literature review

This paper deals with the simulation and green processing of zeolite 4A and zeolite 5A manufacturing. The literature review focus on the methods of manufacture of these two synthetic zeolites.

A. Hydrogel process

A zeolite gel is defined as a hydrous metal aluminosilicate prepared from aqueous solution, reactive solids, colloidal sols, or reactive aluminosilicates such as the residue structure of meta-kaolin and glasses. For hydrogel process, the typical starting raw materials include an aqueous solution of sodium silicate (Na_4SiO_4), H_2O, Al_2O_3-$3H_2O$ to form sodium aluminate ($NaAlO_2$), and sodium hydroxide [13]. These are mixed with water in a tank, followed by gel make-up reactor, then gel aging and crystallization, as shown in Figure 1.

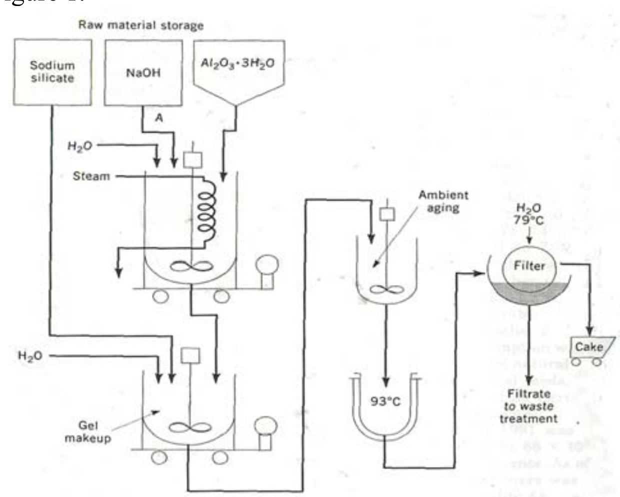

Figure 1 Hydrogel process flow sheet for the manufacture of zeolite 4A from reactant hydrogel [14]

The reactions are:

Sodium Aluminate formation
$2NaOH + Al_2O_3\text{-}3H_2O \rightarrow$
$2NaAlO_2$ (Sodium Aluminate) + $4H_2O$

Zeolite 4A Gel Formation
Na_4SiO_4 (Sodium silicate) + $NaAlO_2$ (Sodium Aluminate) + $H_2O \rightarrow 2Na_2O\text{-}Al_2O_3\text{-}1.75SiO_2\text{-}70H_2O$ (Zeolite 4A Gel)

Water removal
$2Na_2O\text{-}Al_2O_3\text{-}1.75SiO_2\text{-}70H_2O$ (Zeolite 4A Gel) $\rightarrow$
$2Na_2O\text{-}Al_2O_3\text{-}1.75SiO_2\text{-}6H_2O$ (Zeolite 4A dry) + $64H_2O$

After zeolite 4A crystals are formed, wet zeolite passes through a filter to remove part of water, and then the final product zeolite 4A is obtained.

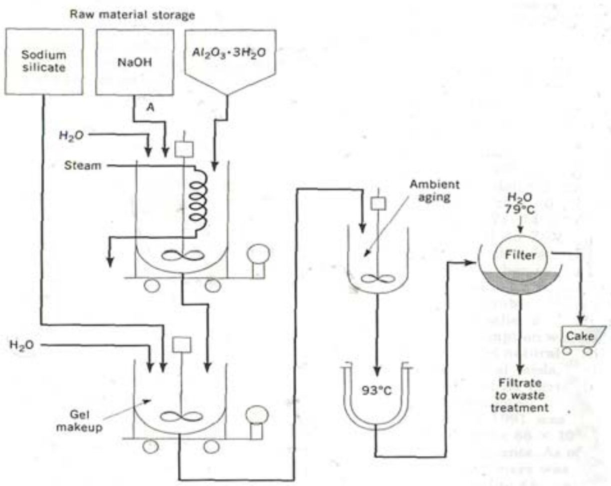

Figure 1 Hydrogel process flow sheet for the manufacture of zeolite 4A from reactant hydrogel [14]

Considerable research has been done on the mechanism of zeolites synthesis [2- 20], the mechanism of zeolite synthesis remains ambiguous. Some studies of the kinetics of zeolite A synthesis found that the process start with an induced period of nucleation immediately followed by a stage of fast crystal growth. The zeolite formation was claimed to be an autocatalytic reaction, which means zeolite A need to be introduced as crystallization seed. The crystallization mechanism for batch process was given by Kerr [14]. Liu [15] studied the kinetics mechanism of zeolite crystallization, and proposed mathematical models for different situations.

B. Clay conversion process (Kaolin conversion process)

The starting material for this process is Kaolin ($Al_2Si_2O_5(OH)_4$), which is usually dehydroxylated to meta-kaolin ($Al_2Si_2O_7$) [30]. This is done by air calcinations at 500 – 600 °C, to form meta-kaolin according to the reaction:
$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$ (at 550 °C)
Kaolin Meta-kaolin

At high temperature (1000 – 1100 °C) the meta-kaolin is broken down to calcined kaolin, called mullite ($Si_2Al_6O_{13}$), and SiO_2 called cristobalite.
$3Al_2Si_2O_7 \rightarrow Si_2Al_6O_{13} + 4SiO_2$ (at 1000-1100°C)
Figure 2 shows the flow sheet of the kaolin conversion process,. The flow sheet does not include the dehydroxylation of kaolin; Mullite and cristobalite are reacted with caustic soda and water in a gel make-up tank to produce zeolite 4A gel. The reaction is:

$12NaOH + 204H_2O + Si_2Al_6O_{13} + 4SiO_2$ (200 F) $\rightarrow$
3 ($2Na_2O\text{-}Al_2O_3\text{-}2SiO3\text{-}70\ H_2O$)
Zeolite 4A Gels

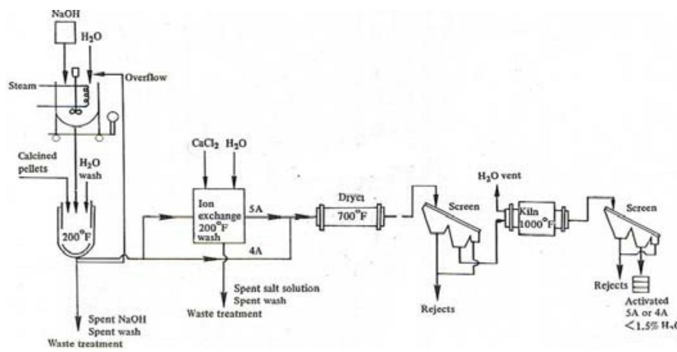

Figure 2 Kaolin conversion process, Process flow sheet for producing zeolite 4A and 5A [2]

To produce zeolite 5A, zeolite 4A gel is fed to an ion exchanger, where it is mixed with calcium chloride and water. In this process some of Na^+ ions in zeolite 4A gel are replaced by calcium ions, Ca^{2+}. The reaction is;

($2\ Na_2O\text{-}Al_2O_3\text{-}2SiO_2\text{-}70H_2O$) (Zeolite 4A Gel) + 0.7 CaCl2 (200 F) $\rightarrow$
$0.7CaO\text{-}0.3\ Na_2O\text{-}Al_2O_3\text{-}2SiO_2\text{-}70H_2O$ (Zeolite 5A wet) + Na_2O + 1.4 NaCl

Wet zeolite 5A will pass through dryer to remove part of the water and form the dry zeolite at 1000 F. The reaction is:
$0.7CaO\text{-}0.3\ Na_2O\ \text{-}Al_2O_3\text{-}2SiO_2\text{-}70H_2O$ (1000 F) $\rightarrow$
$65.5\ H_2O + 0.7CaO\text{-}0.3\ Na_2O\ \text{-}Al_2O_3\text{-}2SiO_2\text{-}4.5H_2O$ (Zeolite 5A dry)

The zeolite 5A dryer product has a particle size distribution (PSD) which has to be incorporated into the process simulation model. The dryer product is introduced into screens to remove undersize and oversize particles. The final zeolite 5A product (with certain PSD) exits from the screens.

C. Element Utilization Efficiency (EUE)

Element utilization efficiency (EUE) or atom utilization efficiency (AUE) are relatively new concepts, introduced to evaluate flow sheet changes that improve green processing. The element efficiency is defined as:

$$EUE = \frac{\text{the molar flow rate of each element in final product Zeolite 4A or 5A}}{\text{the total molar flow rate of each element fed in}}$$

Changes in the flow sheet that would increase the EUEs would enhance green processing and reduce undesirable waste stream.

D. Heat Integration

Heat integration involves the use of hot exit streams that need to be cooled to heat cold streams that need to be heated. However heat exchangers (and capital costs) are needed. A validated simulation model is a valuable tool in assessing the economic benefits of the heat integration. In the kaolin conversion process, considerable heat can be recovered. The required heat exchanger surface area and heat duty are obtained using a heat exchanger block in ASPEN Plus. Based on Qi [21] the heat transfer coefficient was assumed to be 100 $W/m^2 \cdot K$.

II. Goal/Objectives

The overall goal of this study is to simulate the manufacturing processes of zeolite through hydrogel process and via kaolin conversion process, and suggest approaches to apply green processing technology into the process. The objectives are:

- Develop simulation packages that characterize technical performance of each process.
- Evaluate atom efficiency and processes that would improve the element utilization efficiency.
- Implement heat integration as a tool for energy efficiency.
- Do preliminary cost estimation.
- Evaluate the financial soundness of the above green processing technologies.

III. Approach/Methodology

Three simulation packages were used. These are:

a) ASPEN Plus from ASPEN Technology. Inc
b) EES (Engineering Equation Solver) from F-Chart
c) Microsoft Excel. This was mainly used for costing calculations, overall mass balance check, elemental efficiency, and heat integration calculations.

A. EES Application

EES was used to verify the consistency of the technical data obtained from literature. Those information include Kerr's model [14] for batch process of producing zeolite A, Liu's model [15] for continuous processes of forming zeolite A, and Hu's synthesis kinetics model [16, 17] of zeolite A. Based on EES results [30], ASPEN Plus package was used to study those kinetic models. The simulation results of the present work were in very good agreement with literature values, thus validating our models. The models developed and tested in this study can only be used to simulate zeolite A manufacturing. Attempts to compare the present model with the kinetics models of Dufour [18, 19] and Freund [20] resulted in large differences [30].

B. Application of ASPEN Plus

ASPEN Plus simulation package is used to model the production of Zeolite 5A through kaolin conversion, and the manufacture of Zeolite 4A via the hydrogel process. ASPEN Plus is also used to compute the heat duty and heat exchanger area during heat integration. To simplify the simulation, the properties of all materials were assumed to be the same as water, and the thermodynamics to follow ideal system. An important feature in ASPEN Plus is its capability to handle gas, liquid and solid stream. Conventional (gas/liquid) components are simply denoted by "CV" or "CONV". The conventional components in the two processes are:

Kaolin conversion process: H_2O, air
Hydrogel process: H_2O

The zeolites manufacturing flow sheet (Figure 2) include two types of solids. The first type is conventional inert solids (CISLD). These can be in chemical equilibrium with conventional gas and liquid components, and have a molecular weight, examples of these solids are:

Kaolin conversion process: Al_2O_3, SiO_2, mullite ($Si_2Al_6O_{13}$), NaOH, Na_2O, $CaCl_2$, CaO, NaCl

Hydrogel process: Al_2O_3, SiO_2, NaOH, Na_2O, Na_4SiO_4(Sodium silicate), $NaAlO_2$ (Sodium aluminate)

The second type is non-conventional solids (NC). These solids could be heterogeneous substances that can react chemically with conventional CISOLIDS. Examples of the "NC" solids

Kaolin conversion process: Kaolin, zeolite 4A Gel, Zeolite 4A, Zeolite 5A
Hydrogel process: Zeolite 4A Gel, Zeolite 4A product

The first step in any reaction of an "NC" solid is to dissociate the solid into conventional inert solids or conventional liquid and gas. For example:

Kaolin (Molecular weight 258.16) = $Al_2O_3 + 2SiO_2 + 2\ H_2O$.
The molecular weight was calculated from the kaolin formula.

In addition, ASPEN Plus allow for particle size distribution (PSD) of solid streams, both conventional (CISLD) and non-conventional (NC). The solids with PSD in the model of this study are

Kaolin conversion process: Zeolite 5A product
Hydrogel process: Zeolite 4A product

The simulation of the hydrogel process involves four steps (Figure 3):

1. Sodium Aluminate Formation (Circled in red color dash line)
2. Zeolite 4A Gel Formation (Circled in blue color dash dot line)
3. Zeolite 4A Gel Aging and Crystallization (Circled in green color dot line)

4. Zeolite 4A Gel water removal (Circled in yellow color long dash dot dot line)

Each step is in agreement with flow sheet of zeolite 4A gel manufacturing via hydrogel process (Figure 3).

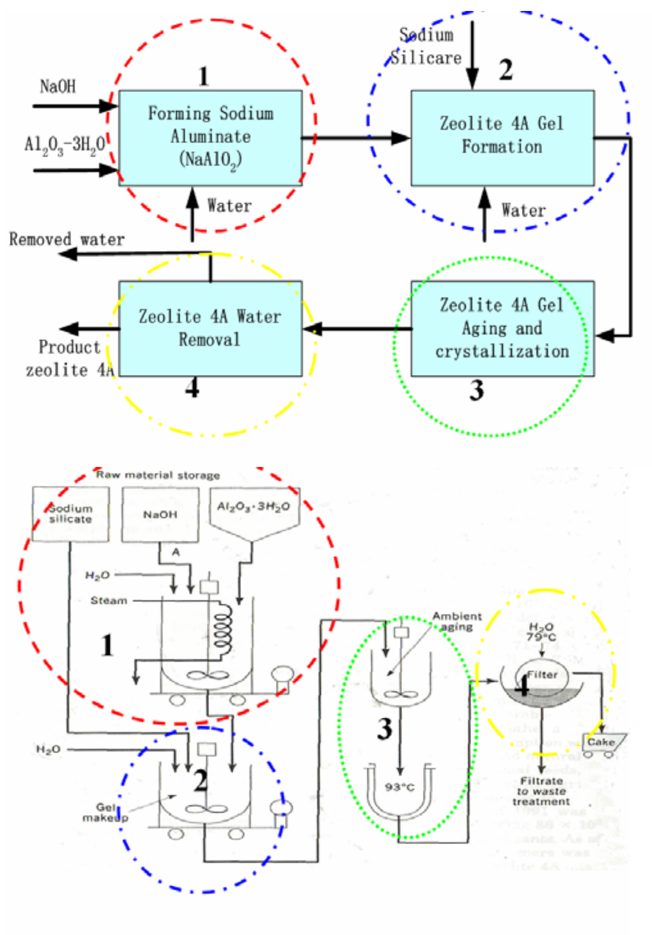

Figure 3 The relationship between ASPEN simulation sequence (top diagram) (before materials recycling) and actual flow sheet of zeolite 4A manufacturing through hydrogel process (bottom diagram).

One of the important of aspects of green processing is to improve the EUE. Recycling a number of streams was proposed to accomplish this, as shown in Figure 4.The current model was used to characterize the effect of the recycle. Attempts to do heat integration to improve energy efficiency in this hydrogel process were not successful. This is because of the relatively low temperatures encountered in the hydrogel process compared to the kaolin conversion process. Careful study of the simulation models results of the hydrogel process flow sheet indicated that there was a large amount of extra water that can be recycled. Using the present model the improvement in the hydrogen and oxygen EUEs can be assessed. Figure 4 shows our proposed recycling of water to improve element utilization efficiency, and make the process greener. Still, fresh water has to be fed in to start the plant, and as make-up.

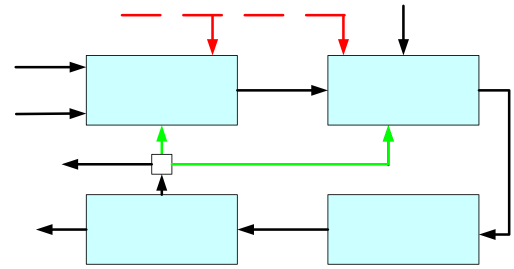

Figure 4 ASPEN simulation sequences (after materials recycling) for hydrogel process

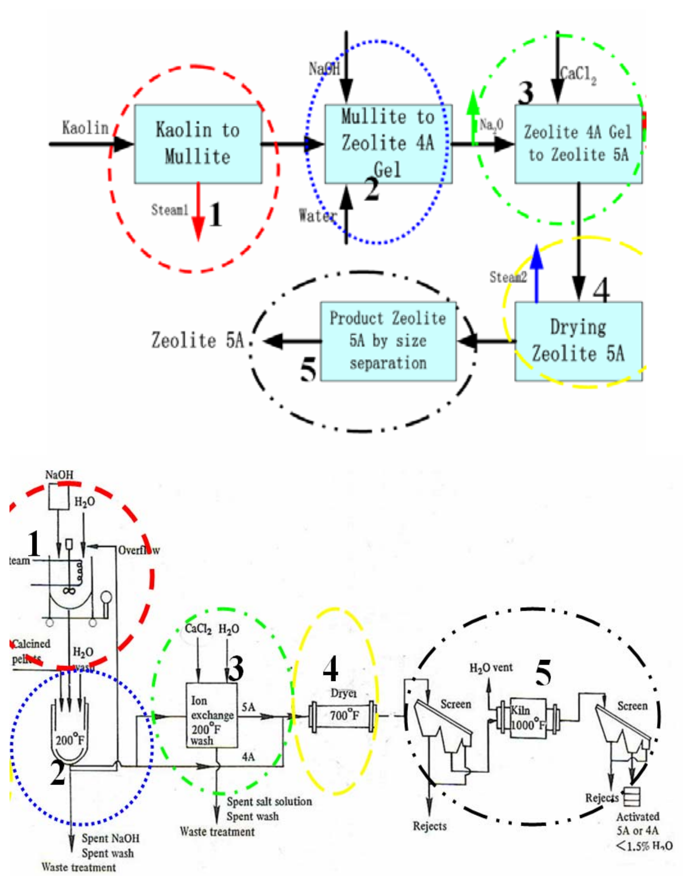

Figure 5 The relationship between ASPEN simulation sequence (top diagram) (before materials recycling) and actual flow sheet of zeolite 5A manufacturing through kaolin conversion process (bottom diagram).

In the kaolin conversion process, both the actual flow sheet and the ASPEN simulation flow sheet include five parts (Figure 5). These are:

1. Kaolin to Mullite (Circled in red dash line)
2. Mullite to Zeolite 4A Gel (Circled in blue dot line)
3. Zeolite 4A Gel to Zeolite 5A (Circled in green dash dot line)
4. Zeolite 5A drying (Circled in yellow long dash line)
5. Zeolite 5A product size separation (Circled in black long dash dot dot line)

Kaolin is modeled as a non-conventional component (NC). The intermediate reactions taking place in the model may be different from the reactions in the literatures. However the final products are the same. For example, step 1 is producing mullite from kaolin, kaolin is first converted to meta-kaolin at 550 C then the meta-kaolin is converted to mullite at 1000 – 1100 C). The following reactions take place.

$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$ (at 550 °C)
Kaolin Meta-kaolin

$3Al_2Si_2O_7 \rightarrow Si_2Al_6O_{13} + 4SiO_2$ (at 1000-1100°C)
Meta-kaolin Mullite Cristobalite

These two reactions can be combined into one reaction taking place at (at 1000-1100°C),
$3Al_2Si_2O_5(OH)_4 \rightarrow Si_2Al_6O_{13} + 4SiO_2 + 6H_2O$
Kaolin Mullite Cristobalite

The reactions in ASPEN Plus dissociate kaolin ($3Al_2Si_2O_5(OH)_4$) into to SiO_2, Al_2O_3 and H_2O, then SiO_2, and Al_2O_3 react to form mullite, i.e.,

$3Al_2Si_2O_5(OH)_4 \rightarrow 3Al_2O_3 + 6SiO_2 + 6H_2O$ (at 550 °C)
$3Al_2O_3 + 6SiO_2 \rightarrow Si_2Al_6O_{13}$ (mullite)

Similar approach was used in the simulation of hydrogel process.

Figure 6 shows our proposed recycling of materials (water, steam, and Na_2O) to improve element utilization efficiency, and make the process more green. As more water is recycled, the fresh water feed decreases.

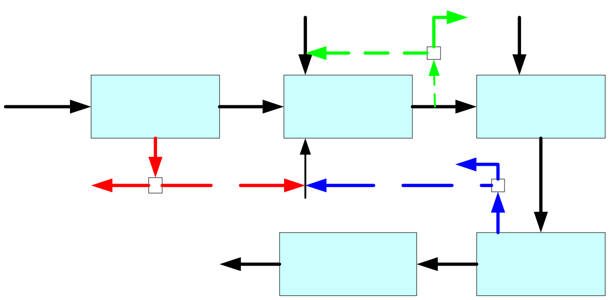

Figure 6 ASPEN simulation sequences for kaolin conversion process with suggested recycling to improve atom efficiency

The Kaolin process involves high reaction temperatures. This provides the potential of heat recovery and integration. The effect of heat integration on cost was studied.

C. Data Exchange between ASPEN Plus and M/S Excel

ASPEN Plus has the capability (through "calculator" block) to dynamically export and import variables to M/S Excel. This permits the use of Excel to do additional calculations that are not readily available in ASPEN Plus. The following computations were done through the data exchange between ASPEN Plus and Excel:

Kaolin conversion process:

1. Calculate element utilization efficiency.
2. Check element balance over the whole process flow sheet.
3. Heat integration-costing evaluation.
4. Calculation of capital, operating, raw materials and the annual cost, as well as the cost per pound of product.
5. Generate graphs of element utilization efficiency, heat integration and costing.

D. Model validation

The followings were done to validate the ASPEN Plus model:

1. Checked that the mass balance for each element is satisfied.
2. Assumed zero conversion in all reactors and confirmed the element balance.
3. When stream recycling is done the case of a zero recycle fraction was run in the model and the results were identical to those of flow sheet without recycle.

E. Preliminary cost Estimation

Preliminary cost included the flowing elements: labor cost, raw materials cost, operating cost, equipment cost and annual fixed cost. All of raw materials price information was obtained from Chemical Market Reporter [22], the evaluation of equipment cost estimation was based on ASPEN simulation results and Garrett's economic models [23]. Labor cost estimation and operating cost estimation were based on Peters, Timmerhaus's method and data [24-28]. The annual fixed cost was assumed to be 20% of installed cost.

III. Results & Discussion

A. Hydrogel process (for manufacturing zeolite 4A)

1) Elemental Utilization Efficiency Results. In this process, five different atoms are fed in flow sheet. These are Si, Al, Na, O and H. The results of our modelare shown in Figure 7.

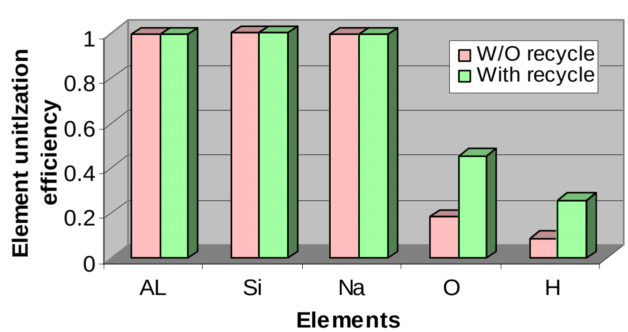

Figure 7 Element efficiency difference between with water recycling and without water recycling (hydrogel process)

The Figure shows high EUEs of Al, Si, Na element (about 99%). The EUEs of O (18.3%) and H (8.6%) indicated that there was room for improved green processing. A careful review of the whole process revealed that there were large amount of water that can be recycled. This would improve hydrogen and oxygen utilization efficiency. The proposed recycling scheme is shown in Figure 4. Figure 7 show that the hydrogen utilization efficiency increases from 8.6% to 25.8%, and the oxygen efficiency increased from 18.3% to 25.8%.

2) Effect of plant capacity. Figure 8 shows the computed cost zeolite 4A in \$/lb versus the plant capacity (metric tons per year). Increasing the plant capacity drops the zeolite product cost from 31 cent to 16 cents/lb. At some capacities (e.g., 6,200 and 19000 metric tons/y), the cost increases slightly, when capacity increases. This is because the equipment cost (and size) are discrete (non-continuous) functions of the plant capacity. Figure 8 also shows that the raw materials cost play the most important role. As the plant capacity increases, as the product cost decrease, while the raw materials cost per pound of product remains the same. This makes the contribution of raw materials to the total cost increase from 46% to 88%. Meanwhile profit margin increases when plant size grows due to the drop in the product cost (\$/lb).

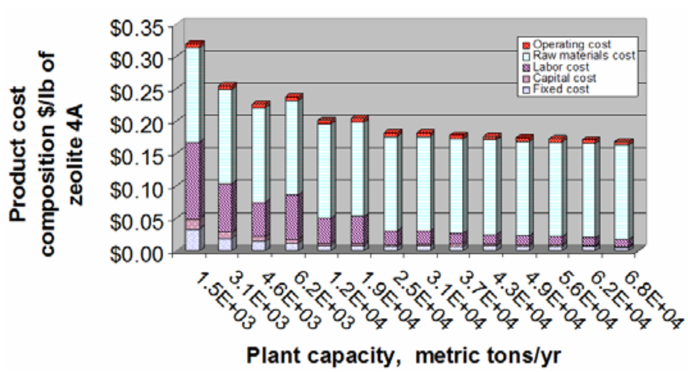

Figure 8 Effect of plant sizes on cost of zeolite 4A in hydrogel process

B. *Kaolin conversion process (for manufacturing zeolite 5A)*

To make this process more efficient, the present study found that there were several streams that can be recycled. These included extra water and extra Na_2O. The effect of those recycled streams on the EUEs was evaluated by the present simulation models. At the same time, heat integration was also modeled resulting in energy savings and cost reduction.

1) *Elemental Utilization Efficiency Results*. In the Kaolin process, The EUEs of six elements (Si, Al, Na, Ca, H, and O) were studied and evaluated. The results are shown in Figure 9. It shows high EUEs of Si, Ca, and Al, at about 92%. This is in agreement with earlier study [17-20]. The EUEs of Na, H and O were low. We proposed and evaluated the effect of recycling water and sodium oxide on the EUEs. As a result the EUE of sodium (Na) almost doubles from 13.9% to 27.7%. Hydrogen (H) and oxygen (O) EUEs show considerable improvement (H from 5.8% to 92.4%, O from 14.3% to 92.5%). Figure 10 displays the computed mass (in pounds) of generated Na_2O and water per pound of zeolite produced, both before and after recycle would be implemented. The present model shows that large amounts of sodium and wastewater will not be released to the environment, as shown in Figure 10. This is an example application of pollution prevention (P2), and the benefit of the present model.

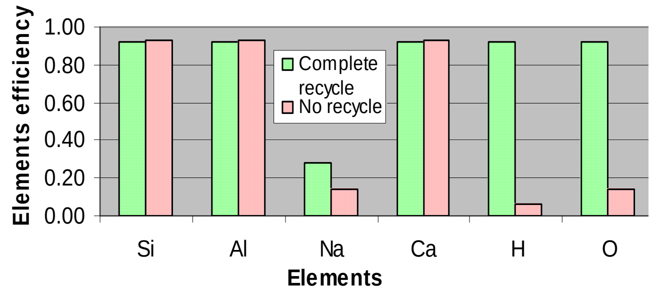

Figure 9 Element efficiency difference between with recycling and without recycling (kaolin conversion process)

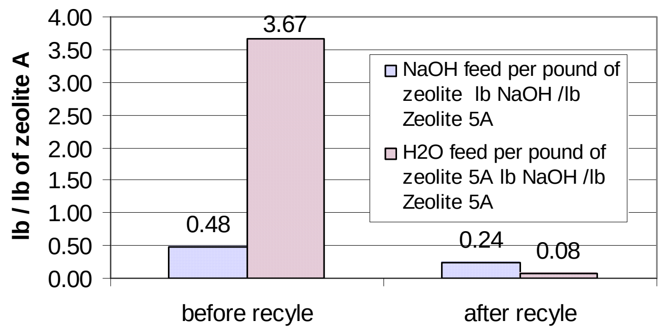

Figure 10 Effect of Recycle on wastewater and Na_2O generated in the Kaolin manufacturing process.

2) Preliminary cost estimation. The kaolin conversion process is operated at higher temperatures than the hydrogel process. The temperature can reach 550°C – 1100°C when kaolin is calcined to Mullite. There is a large amount of heat that can be recovered. Figure 11 shows that, when plant capacity is increased from 2,100 to 67,000 mt/y, the cost decreases with or without heat recovery. The zeolite 5A cost dropped from 42 cents to 34 cent per pound of zeolite 5A without heat integration

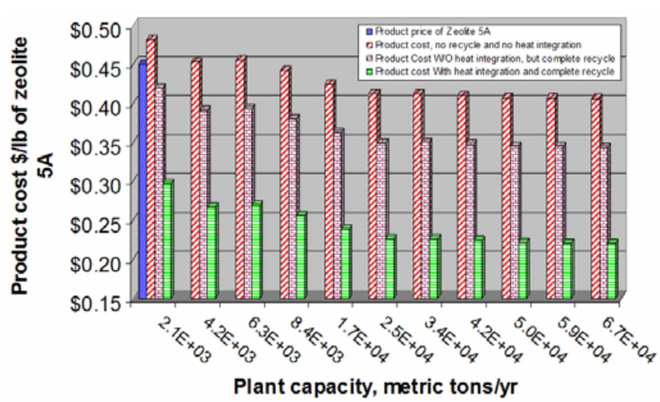

Figure 11 The effects of heat recovery on cost under different plant capacity

. When heat integration was included, Figure 11 ahows the product cost of the 67,000 mt/y plant to drop to 22 cents/pound of zeolites 5A. Therefore the operating cost can be reduced by 12 cents/lb of zeolites 5A (about 35% drop) through heat integration.

The results of Figure 12 show that without heat integration, operating cost and raw materials cost are two biggest parts in total cost.

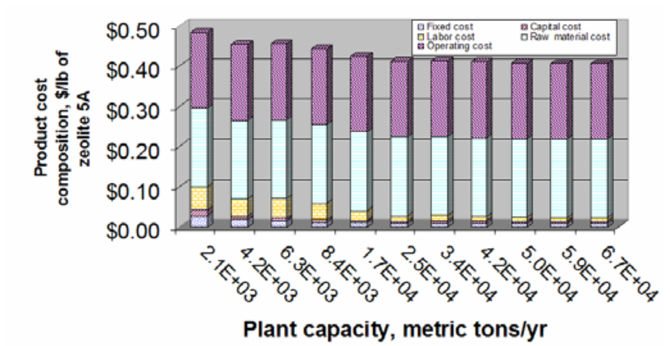

Figure 12 Product zeolite 5A cost composition, without heat recovery.

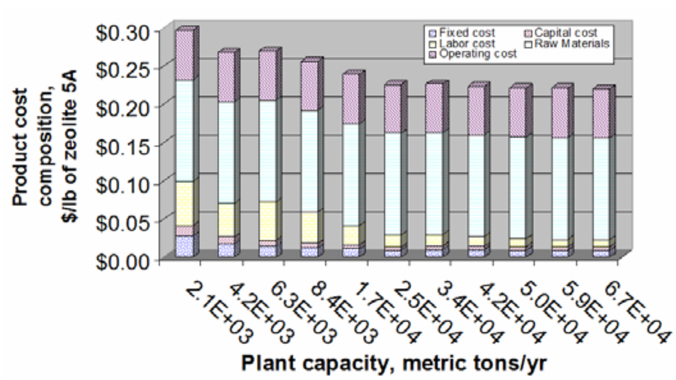

Figure 13 Product zeolite 5A cost composition with heat recovery.

When heat integration is implemented in the present models the results are shown in Figure 13. For each plant capacity the model estimates the contribution of labor cost, raw materials costs, operating costs, equipment cost and fixed cost to the production cost of zeolite 5A in $/lb. Figure 13 shows that the contribution of operating costs decrease, and the raw material costs become the major contributor to the total cost. Therefore, to improve the economics further, the zeolite production facility may need to consider how to obtain the raw materials at a lower cost.

IV. Conclusions

1. Computer simulation of zeolites production is a feasible and cost effective tool to optimize the manufacturing process. It has been used to study the application of green processing and pollution prevention (P2) to improve the EUEs and decrease the release to environment.

2. In the hydrogel process that produces Zeolite 4A water recycling can improve Hydrogen and Oxygen utilization efficiency.

3. In the kaolin conversion process to produce Zeolites 5A, hydrogen and oxygen utilization efficiency can be improved via water and steam recycling, Oxygen and Sodium utilization efficiency can be improved through Na_2O recycling.

4. Heat integration can play an import role in kaolin conversion process of producing zeolites 5A, resulting in a reduction in the operating cost of about 12 cents/ lb of zeolite 5A (about 35% cost reduction).

5. Increasing the plant capacity reduces the total cost of products for both zeolites 4A and zeolites 5A.

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