Zeolites in Agriculture

June 14th, 2017
What are zeolites?

- Are synthetic or natural- from volcanic ash and rock reacting with alkaline groundwater
- Are crystalline aluminosilicates
- Infinite porous structure
  - Three-dimensional frameworks of silicon-oxygen (SiO\(_4\)) tetrahedral
  - Aluminum inclusion causes slight deficiency in positive charge
  - Forms channels that allow ions and molecules to pass in and out of zeolite structure
Importance of Cation Exchange

- Can accommodate large variety of cations, depending on species of zeolite
  - $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$
  - Polarity affinity
- Selective sorting of molecules based on size-controlled by dimensions of the pores
- Cations loosely held and can be readily exchanged for other cations (aqueous environment)…..SLOW RELEASE!
What This Means

- Because of this unique property, zeolites can be used in a multitude of ways including:
  - ion exchange, filtration, odor removal, sieving chemicals, water and gas absorption
  - Highly involved in biochemical processes
- Environment dependent (think saturated field)
  - Efficiency changes
- Problems with misleading and conflicting research and results
  - Due to ‘zeolite’ being coined for many different minerals with differing characteristics and chemical make-up
    - Different purities
    - Differing affinity for cations
Pollution Control
- Radioactive Waste Treatment
- Waster Water Treatment
- Flue Gases Treatment
- Oil and Lubricant Spill Treatment
- Land Fill Area Treatment

Energy
- Purification of Natural Gases
- Coal Extraction
- Extraction of Petroleum Products

Agriculture
- Soil Conditioner
- Fertilizer Additive
- Soil Pollution Control
- Feed Additive
- Pellet Binder
- Animal Litter
- Organic Waste Treatment
- Aquaculture

Mining & Metallurgy
- Mining
- Metallurgy

Others
- Paper
- Construction
- Sanitary
- Detergent
- Pools and Spas
- Filtration Material
- Landscaping and Gardening
- Aquarium Materials
Use in Animal AG

- 1960’s through 1990’s sparked interest
- Resurgence in research as feed additive and preventative for metabolic diseases
  - Specifically clinoptilolite
- Using zeolite has been proven to increase metabolizable energy utilization and ADG in swine and poultry (G. C. Shurson, P. K. Ku, E. R. Miller and M. T. Yokoyama)

- Looking forward - Research has shown:
  - Zeolite minerals may absorb excess ammonia after feeding and release this gradually when rumen concentrations are low
  - Some improved digestion and metabolism when zeolite added to diet
  - Enhanced microbial growth and function due to clinoptilolite maintaining suitable levels of ammonia
Prevention/Treatment Of Clinical Disease

- Efficacious in the prevention of ammonia and heavy metal toxicities, poisonings as well as radioactive elements uptake and metabolic skeletal defects.

- Use as mycotoxin-binding adsorbent - shown as primary material or after specific minor changes to basic surface properties (Tomasevic-Canovic, M. et al. 2002)
  - Secondary metabolites produced by microbes of fungi origin
  - Zeolite binds -> decreases bioavailability
  - Research shows zeolite effectively binds mycotoxins containing polar groups, ex- alfatoxins
Prevention/Treatment Of Clinical Disease

  - Milk fever - reduced the bioavailability of dietary Ca and efficiently protected against milk fever, by stimulating Ca-homeostatic mechanisms prior to parturition.
    - Both synthetic and clinoptilolite (natural)
  - Ketosis - suggested that clinoptilolite improved the energy status of the cows, either via prepartum enhancement of propionate production in rumen or through the improvement of the post-ruminal digestion of starch.

- Prevention of toxicities
  - White and Ohlrogge first stated that ammonium ions formed by the enzyme decomposition of non-protein nitrogen were immediately ion exchanged into the zeolite structure and held there for several hours until released by the regenerative action of Na+
  - Lead to research of rumen and ammonium concentration
Sub-acute Disease (Acidosis)

- Ruminal pH fluctuates - determined by dynamic balance between the intake of fermentable carbohydrates, buffering capacity of the rumen, and rate of acid absorption from the rumen.

- Most commonly defined as repeatedly occurring prolonged periods of depression of the ruminal pH to values between 5.6 and 5.2.
  - Caused by VFA accumulation with/without persistent lactic acid accumulation.
  - Ruminal papillae increase in length when cattle are fed higher-grain diets.

- Depressed dry-matter intake becomes especially evident if ruminal pH falls below ~5.5.
  - Rumenitis could cause pain and also contribute to intake depression during subacute ruminal acidosis.

- This would clinically be subacute acidosis.
Acute Acidosis

- Conditions worsen as ruminal carbohydrate fermentation shifts to lactate production at lower ruminal pH
  - Mostly due to *Streptococcus bovis* proliferating and shifting to lactate instead of VFA production
- Lactate stays in the rumen longer and contributes to the downward spiral in ruminal pH
- Microbe populations shift
  - Lactate-utilizing bacteria, such as *Megasphaera elsdenii* and *Selenomonas ruminantium*, begin to proliferate
  - Slower turnover time of lactic acid users than synthesizers
  - Reduces the number of species of bacteria in the rumen
Downward Spiral

- Low ruminal pH may lead to rumenitis, erosion, and ulceration of the ruminal epithelium.

- A reduced rate of VFA absorption causes ruminal pH to drop for two reasons: ruminal VFA accumulate and bicarbonate input from the blood stream is decreased.

- Once the ruminal epithelium is inflamed, bacteria may colonize the papillae and leak into the portal circulation.
  - These bacteria may cause liver abscesses, which may eventually lead to peritonitis around the site of the abscess.
Table 1: Main differences between the two different clinical forms of ruminal acidosis [5].

<table>
<thead>
<tr>
<th></th>
<th>Ruminal acidosis</th>
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<tbody>
<tr>
<td></td>
<td>Acute</td>
<td>Subacute</td>
</tr>
<tr>
<td>Presence of clinical signs</td>
<td>Yes</td>
<td>Maybe</td>
</tr>
<tr>
<td>Mortality</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Ruminal changes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) Rumen pH</td>
<td>Below 5</td>
<td>5.0–5.4</td>
</tr>
<tr>
<td>(2) Lactic acid</td>
<td>Increase (50–120 mM)</td>
<td>Normal (0–5 mM)</td>
</tr>
<tr>
<td>(3) Volatile fatty acids (VFA)</td>
<td>Decrease (&lt;100 mM)</td>
<td>Increase (150–225 mM)</td>
</tr>
<tr>
<td>(4) Gram negative bacteria</td>
<td>Decrease</td>
<td>Normal</td>
</tr>
<tr>
<td>(5) Gram positive bacteria</td>
<td>Increase</td>
<td>Normal</td>
</tr>
<tr>
<td>(6) <em>Streptococcus bovis</em></td>
<td>Increase</td>
<td>Normal</td>
</tr>
<tr>
<td>(7) <em>Lactobacillus</em> spp.</td>
<td>Increase</td>
<td>Normal</td>
</tr>
<tr>
<td>(8) Lactic acid producers</td>
<td>Increase</td>
<td>Increase</td>
</tr>
<tr>
<td>(9) Lactic acid consumers</td>
<td>Decrease</td>
<td>Increase</td>
</tr>
<tr>
<td>Blood parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) Blood pH</td>
<td>Low</td>
<td>Borderline</td>
</tr>
<tr>
<td>(2) Bicarbonate</td>
<td>Low</td>
<td>Borderline</td>
</tr>
<tr>
<td>(3) Lactate</td>
<td>Increase</td>
<td>Normal</td>
</tr>
</tbody>
</table>

Metabolic Diseases

- Rumen pH controlled by affinity for ammonia and slow release
  - Creates stable rumen-microbe environment
  - Could lead to decrease in acidosis

  Ammonium ions formed by the enzyme decomposition of non-protein nitrogen (excess rumen ammonia)

  Exchanged into zeolite structure
  
  Several hours pass
  
  Held in zeolite structure

  Animal consumes feed
  
  Na⁺ enters rumen after feeding through saliva

  pH stays stable

  Ammonium released by regenerative action of Na⁺
Narrow Scope

- Objective use
- Synthetic versus Natural
- Where and how the zeolite was formed
  - Northern hemisphere natural zeolites were formed when molten lava came in contact with sea water, thereby 'loading' the zeolite with Na (sodium) ions

- Accessibility
  - Clinoptilolite (commonly found natural zeolite)
  - Used as a soil treatment - potassium vs nitrogen
  - Water moderators, in which they will absorb up to 55% of their weight in water and slowly release it under the plant's demand
  - Added to chicken food, the absorption of water and ammonia by the zeolite made the birds droppings drier, less odoriferous and hence easier to handle
Clinoptilolite

- Studies have shown rumen ammonia was lowered when added to diet (Hemken, R. W. et al) (Bergero D.)
  - Important for diets high in nonprotein nitrogen
- Efficiency of fed cattle not fully understood - conflicting results (Hutcheson, D. P. vs Kelly J. Sanders, C. Reed Richardson and Steve Harper)
  - Different composition = different levels
    We understand effects on the rumen - but not efficiency!!

ADG, DMI, Carcass Characteristics, Disease

https://www.daf.qld.gov.au

http://www.gourmetpasturebeef.com/
Leads to Current Study......

- Can increased efficiency of fed cattle be achieved through zeolite feed additive
  - Multiple factors play a role including controlling disease and diet analysis
  - Look at what percent of diet creates the most efficient environment

If clinoptilolite can reduce sub-acute acidosis

+ Statistical differences between control and treatments for ADG, DI and carcass characteristics

= Improved efficiency in fed cattle using a zeolite feed additive
Zeolite Study

- Using Clinoptilolite
- Looking at increased efficiency in fed cattle
  - Sub-acute acidosis through liver abscesses
  - ADG, Daily Intake, DMI, Feed Conversion and Nutrient Composition
- 4 treatment groups: 1 control, .5%, 1% and 2% of fed diet
- 80 steers per treatment in 8 replicates of 10
Looking Forward

- Understand compositional effects among differing zeolite species.
  - Implications of varying amounts
- The European Union has approved clinoptilolite as a binding, anti-aggregating and feed additive for cattle, swine, poultry, and salmon.
- Increased comprehension on use as a buffering agent for reducing metabolic problems.
- Look at environmental approach with loaded manure and field application.
- Further investigate any changes in body composition and carcass characteristics.

Thoughts???

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Thanks!!