Application of Apatite II™ to Copper Remediation in the Dairy Industry of New Mexico and the Western States

Problem Statement

The states of Texas, New Mexico, and Colorado have been in litigation over water rights since before 2002, yet one industry that these states have been trying to attract is the dairy industry. The dairy industry creates great community wealth through both employment and money which trickles down to the many service businesses that maintain the dairies' infrastructure, feed its owners and employees, and fulfill all other consumption needs. Contaminated dairy effluent water produced from daily operations is fast becoming a problem for the industry. As States tighten environmental standards, the dairies tend to migrate towards States with more tolerant standards, i.e. the recent migration from California (where home encroachment encourages enforcement of environmental controls) to Eastern New Mexico and West Texas, and subsequently to Oklahoma as New Mexico and Texas begin to enforce environmental regulations.

Figure 1. An Evaporative Pond.

The traditional means of dealing with dairy effluent water include 1) simply place the water in evaporative ponds or lagoons (*dry dairies*) allowing it to enter into the atmosphere as water vapor (Figure 1), or 2) using the water as irrigation water with center pivot systems (*wet dairies*). An average sized dairy is permitted to discharge 40,000 gallons of effluent water into evaporative lagoons each day and larger dairies are permitted to discharge 100,000 gallons of water each day. Unfortunately, many of the dairies' evaporative lagoons are losing efficiency and their capacity has been reduced by an average of 30% due to the accumulation of solid waste. Most lagoons are now rapidly losing freeboard defined as the distance between the water surface and the regulatory limit of the lagoon which is two feet below the lagoon's edge.

The accumulation of solids results from an accumulation of copper ion (Cu^{2+}) in the lagoon water, a byproduct of the copper sulfate solutions used in the cattle footbaths that the animals walk through every day (Figure 2). Copper sulfate is used to prevent the development of foot warts and other hoof diseases which are highly contagious, lame cattle, and lead to significant economic

Figure 2. Copper sulfate foot baths for cattle.

loss for the dairies. Unfortunately, this same copper, when washed daily into the evaporative lagoons, also kills the microbes that digest the solids. If this water is subsequently used for irrigation, the copper also accumulates in the soils. *Copper burn* has begun to appear in many fields.

There are 206 dairies registered with the New Mexico Dairy Producers Association (NMDPA) and many times this number in other states. Of those, 106 NM dairies are categorized as noncompliant by the New Mexico Environment Department (NMED), and the number is growing. NMED states that excessive effluent discharge and leaking evaporative lagoons are the main causes of non-compliance, and this is directly related to copper contamination. As lagoons loose their capacity, many more members of the dairy industry will face problems related to lagoons exceeding their holding capacity for solids, complaints related to odor, and environmental complications related to the discharge of excess solids and copper in land application areas.

A woman owned small business in Carlsbad, NM, in cooperation with AgVentures, LLC in Portales, NM, and in collaboration with New Mexico State University Department of Microbiology, have developed a method for reducing both the copper and the solids in the lagoon water. The method uses an inexpensive, benign, natural additive derived from fish bones (Apatite II™) to sequester the Cu and stimulate biodegradation of the solids. The efficiencies are quite large and the process is quite rapid. This method also treats many other problems in these waters such as high salts and other toxic metals. This technology can be utilized by the entire dairy industry with no additional regulatory issues.

Description of Dairy Management of Solid Waste

The dairy milking parlor is considered a food service area, and, therefore, must be maintained to a certain level of cleanliness. Because the cows being milked defecate while inside the parlor, the milking parlor itself is frequently cleaned. The removal of animal waste is normally done through a combination of a flush valve and hoses that rinse the solids into a drain system. The water and rinsed solids are discharged into the evaporative lagoons. Most dairies use a solids separator to remove large solids from the rinse water prior to depositing the water in the lagoon. Figure 3 shows a solids separator.

Figure 3. A solids separator prior to discharge into pond.

The solids separated at this stage are scraped out by a tractor and scraper and used as fertilizer for the production of forage crops. The remaining solids and water are then discharged into the evaporative lagoon. Normally solids are digested by microorganisms, either aerobically or anaerobically. Figure 1 shows an evaporative lagoon not impacted by copper, where the microorganisms are digesting the solid waste at an acceptable rate. However, the presence of copper in sufficient amounts kills these microorganisms, just as it does the disease microbes, thus stopping digestion, causing build-up of solids, and making the lagoons ineffective. Figure 4 shows such an copper-impacted lagoon with solids building up on the surface.

Figure 4. A copper-impacted pond with solids accumulation.

Lagoon Remediation Synopsis

Many evaporative ponds in New Mexico have ineffective microbial activity that leads to an accumulation of solids. Figure 4 demonstrates such solid accumulation in a pond effected by copper. The physical configuration of the treatment system can be adapted to any farm-lagoon situation. Wash water leaving the seperator passes through the Apatite II, which can either be containerized or be filling a trench or spillway. The water then enters the pond, removed of copper and biologically active. Apatite II will also be applied to the pond itself to remove copper already in the pond and stimulate microbial activity. The Apatite II can be supplied as a highly porous material, with water conductivities similar to gravel, or it can be crushed to a sand-sized material for spreading in the lagoon or mixing into solids or soils. Collaborations with NMSU microbiologist Geof Smith and geochemist Jim Conca have shown the extreme reactivity of the material with respect to heavy metals and anaerobic microbes.

The Remediation Process

The reactive media developed for this problem is Apatite II™ (U.S. Patent #6,217,775), a biogenically precipitated apatite material that is derived from fish bones and has the general composition:

$$Ca_{10-x}Na_x(PO_4)_{6-x}(CO_3)_x(OH)_2$$

where x <1. There are about 30% to 40% by weight of associated organic materials in the internal porosity of the inorganic structure (Figure 5) primarily collagen with some fats and proteins, an ideal assemblage for biostimulation.

Apatite II works to sequester metals by four general, non-mutually-exclusive processes depending upon the contaminant and the aqueous chemistry. First, Apatite II continuously supplies a small, but sufficient, amount of phosphate to solution to exceed the solubility limits of various metal-phosphate solids such as Pb-pyromorphite and U-autunite. Second, Apatite II dissolution is a strong pH buffering reaction, buffering around neutral (6.5 to 7) through its PO_4^{3-}, OH^-, and substituted CO_3^{2-} groups. The third process is surface chemi-adsorption. Apatite II is an excellent material for non-specific metal adsorption, particularly of the transition metals such as Cu, Cd and Zn, through its uncompensated phosphate and hydroxyl surface groups, and can adsorb up to 5% of its weight by adsorption.

The fourth process is precipitation of insoluble metal phases as a result of chemical changes induced by biological activity. This is the most important process for the diary industry. Biological stimulation of sulfate- and nitrate-reducing bacteria by the Apatite II, followed by precipitation of CuS is the primary mechanism of Cu sequestration in this system. Apatite II supplies both P and readily bioavailable organic material along with the lagoon solids, at low but optimal concentrations for stimulating microbial

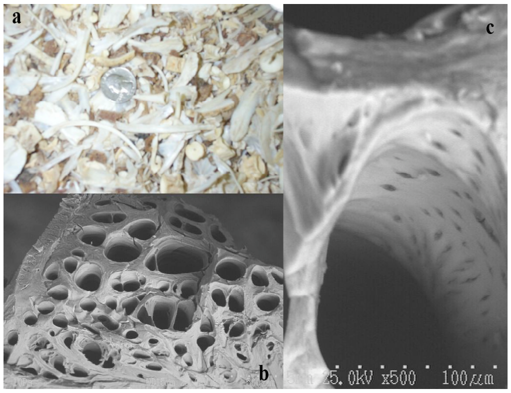

Figure 5. Apatite II showing the various levels of porosity from centimeter to nanometer.

communities. Apatite II contains between 30% and 40% organic material by weight, mostly collagen with various amounts of more soluble proteins, fats, and lipids, such as cholesterol, that remain after processing of the fish bone. The organic substances are slowly leached from the capillary pores and microporosity of the Apatite II, and the equilibrium concentration of P from dissolution of the Apatite II is usually about 1 ppm (mg L^{-1}).

Within the lagoons, a variety of microbial activity occurs which breaks down organic components and carry out conversions among different chemical constituents such as organic nitrogen and nitrate to nitrogen and ammonia, and sulfate reduction to sulfide minerals. These processes are most efficient under anaerobic conditions, using organic carbon from the solids, and can be represented as:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$$

$$Cu^{2+} + HS^- \rightarrow CuS + H^+$$

The CH_2O represents the organics from the solids that serve as both electron donor and carbon source for the reducing bacteria. There are many available microbes in the system that can reduce the sulfate, such as *Entercocci* and *Pseudomonas.* The Apatite II becomes active very quickly, in a matter of hours. The solubility of the CuS is very low, $K_{sp} <10^{11}$; therefore, the stability of the resulting product from a remediation standpoint is excellent, and the concentrations of soluble Cu and S in the lagoon should drop dramatically. The visible sign of a successful equilibrium position is the elimination of solids on the surface of the lagoon, increased biological gas production, reduced water turbidity and increased freeboard.

Previous Results

Figure 6 shows the results, after only one month, of the pilot tests for this application implemented in the same copper-impacted Portales pond shown in Figure 4. This pilot test used only one ton of Apatite II. Some of the Apatite II intercepts outflow from the separator, ensuring adequate contact time and anaerobic conditions to treat new inflow to the lagoon, and the rest of the Apatite II was emplaced directly in the lagoon to treat the existing contaminated water and stimulate the microbial communities that were killed or went dormant as a result of the Cu contamination. After only one month with this small amount of Apatite II, the turbidity has greatly decreased, gas production has dramatically increased, most of the accumulated solids have disappeared from the pond surface (compare figures 4 and 6), and the pond has gained 6 inches of freeboard. This treatment was a beta-site demonstration using a small amount of Apatite II that showed the process works and how fast it works. However, a larger treatment, three to four tons, is estimated to completely remediate the lagoon, and a full demonstration is needed to determine real costs, how long the process works before another treatment is required, e.g., a ton every year, and what O&M is required.

Figure 6. The copper-impacted pond shown in Figure 4 one month after treatment with Apatite II. Turbidity has decreased, gas production has increased, all accumulated solids have disappeared from the surface, and the pond has gained 6 inches of freeboard.

Previous results of Apatite II applied to heavy-metal waste waters in the mining industry, have shown that Pb, Cu, Zn, U and Cd are readily removed from contaminated water and soil by the application of Apatite II, either as a filter medium in a permeable reactive barrier (PRB) or treatment tank, or mixed into contaminated soil. Figure 7 shows results from one of the Apatite II PRB system operating at mines in the Silver Valley region of northern Idaho for the last 5 years. The drop in high metal concentrations to below detection is immediate upon entering the first chamber filled with Apatite II as a result of biostimulation and metal precipitation under anaerobic conditions fostered by the Apatite II. Toxicity studies in these systems using the fat minnow and the invertebrate *C. Dubia* show that the Apatite II changes the water from completely lethal to completely non-lethal. Similar studies at NMSU show that microbial degradation of organic contaminants such as TNT and perchlorate is stimulated by Apatite II even in the presence of heavy metals which are completely toxic to the microbes in the absence of Apatite II.

Market Survey

The general market for lagoon remediation is large, encompassing over 5,000 dairies nationwide, with over 1,000 within a 300 mile radius of Carlsbad. Although all dairies would benefit from the lagoon remediation program, the immediate market in New Mexico and Texas is split into two segments: the most environmentally conscious dairies, and the least environmentally conscious dairies that have few options left to achieve compliance. These number about 100. Five dairies are seriously considering utilizing the proposed technology if this demonstration is successful and there are 53 noncompliant dairies that would use the technology immediately just to maintain their permit status. However, the industry is generally conservative, and several sites will need to be fully remediated before the others will accept the method. Therefore, the five environ-mentally conscious dairies will be used for this demonstration.

The Texas Commission on Environ-mental Quality (TCEQ, the analog to NMED) will shortly be requiring all dairies in the state of Texas to report discharge numbers. TCEQ anticipates that 47%, or roughly 400 of its 850 dairies will instantly fall into noncompliance. Many of these dairies may find other means to achieve compliance, but it is expected that many will require lagoon remediation to retain their permit. The majority of the dairies in Texas are located in west Texas, and are of close proximity to eastern and southeastern New Mexico, an ideal market for the proposed service.

Figure 7. Schamatic of an Apatite II permeable reactive barrier treatment system in northern Idaho treating acid mine drainage with Cu, Cd, Pb and Zn. Field results shown as a function of position within box. Flow rate is 5 gpm, total metals entering are over 100 mg/L (ppm), but total metals leaving are below 0.1 mg/L with Cu, Pb and Cd below the detection limits of 0.002 mg/L.