University of New Hampshire
University of New Hampshire Scholars' Repository

Inquiry Journal 2008

Inquiry Journal

Spring 2008

An Appetite for Apatite: A Study of Black Apatite Adsorption Effects on Organic and Non–Organic Environmental Contaminants

Owen Friend–Gray
University of New Hampshire

Recommended Citation

Friend–Gray, Owen, "An Appetite for Apatite: A Study of Black Apatite Adsorption Effects on Organic and Non–Organic Environmental Contaminants" (2008). *Inquiry Journal*. 5.
https://scholars.unh.edu/inquiry_2008/5

INQUIRY journal

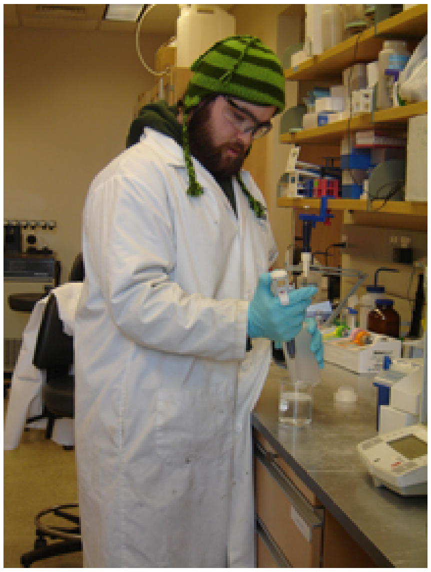
UNH UNDERGRADUATE RESEARCH JOURNAL SPRING 2008

research article

An Appetite for Apatite: A Study of Black Apatite Adsorption Effects on Organic and Non–Organic Environmental Contaminants

—Owen Friend–Gray (Edited by Brigid C. Casellini)

It is impossible to turn on the television or read a newspaper and not hear about environmental contamination. We receive constant warnings of mercury levels in fish, lead paint in old houses, and oil spills leaking into ground water and soil. The major problem with such heavy metals and organic compounds is that they do not break down in the environment. Contaminants that don't break down bio-accumulate, meaning that the contamination will always be there; and the more we add to the environment, the more of a problem it will become.



Owen Friend–Gray at work in his laboratory at Gregg Hall

Currently, various methods are used for treating different types of contaminants, but one all–encompassing method is still out of reach. My research throughout my undergraduate career has focused on trying to adapt these existing technologies and materials to create one treatment method for all of the various pollutants found in contaminated sediment. I was fortunate to be offered this type of research by Dr. Jeffrey Melton when I was a freshman and given a chance to do some real hands–on laboratory work. I was then able to continue this research over the summer between my fourth and fifth semesters thanks to a grant from the Undergraduate Research Opportunity Program. My goal was to discover if apatite, an adsorptive rock, could remove metal and organic contaminants. I was looking for a contaminated sediment panacea.

An Appetite for Understanding Contamination Issues

Mercury and lead are the most commonly talked about heavy metals because they are the most widespread contaminants and affect the largest number of people (Brodkin, 2007). However, many other metals can be just as harmful, such as chromium, copper, zinc, arsenic, and cadmium. Long term exposure to any of these metals can have detrimental effects on humans and animals, ranging from brain damage to birth defects to even cancer and death (Brodkin, 2007).

Organic contaminants are carbon–based and include polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbon (PAHs), among others. PCBs are chemicals used primarily in refrigerant and air conditioning systems, and they are introduced into the environment mostly through improper disposal of refrigeration systems. Exposure to PCBs can lead to painful skin irritation and even extensive liver damage (Carpenter, 2002). PAHs get into the environment from incomplete burning of organics like coal, oil, and gasoline; these chemicals have been linked to cancer and chromosomal abnormalities in infants and adults (Phelps, 2005).

One of the most common areas for these contaminants to collect in is sediment at the bottom of streams and rivers where they are dumped. A method often used to treat this sediment is environmental dredging, a process by which sediment is dug up from the river bed and disposed of in a confined landfill. While this method often works, it can stir up the contaminants and reintroduce them into the water at higher concentrations. It is also not always the most economically efficient or practical method. When a waterway needs treatment, dredging projects are often passed over because the cost is too high or the equipment cannot reach the site. Because of the problems of removing contaminants from the site, *in–situ* (meaning "in place") remediation is used to cut costs and make more sites accessible for treatment. If done properly, in–situ treatment can be more effective than dredging, and it is starting to be used more frequently.

Capping is an in–situ treatment in which the contaminated area is covered with a layer of material such as sand or earth. Large barges or crane ships navigate to the site carrying large amounts of the capping material and pour the substance into the water right on top of the contaminated sediment. This blankets the sediment with a clean surface for plants and animals to use. While this method may slow the contamination's upward flow, it does not treat the issue; it only temporarily masks it. The contamination remains in the ground and can still harm the water and soil around the capping site.

Capping in the Anacostia River in Washington D.C. (Image courtesy of www.uic.edu)

A similar but more effective in–situ treatment is to lay down a reactive cap barrier, which uses adsorption materials to contain the pollutants. In this method, contaminants adhere to the surface of an adsorptive material, where they accumulate to form a thin layer. (They are not a*b*sorbed into the material but a*d*sorbed, that is, bound to its surface.)

An example of reactive capping of river sediments

Reactive caps are like regular caps in the way they are placed on top of the contaminated site, but they differ in that they react with the pollutants and bind them, actually removing the pollutants instead of just covering them up. Reactive caps bind the pollutants because they contain materials like granular activated carbon or apatite, which adsorb the pollutants (Gonzalez, 2003). Once the cap is saturated with the contaminant, it can either be covered with more reactive capping material or dredged and disposed of in a landfill.

Activating a substance such as carbon is done by heating the material to very high temperatures, thus reforming the surface and making it larger so that more of the contaminants can bind to it. While activated carbon can adsorb organics and some metals, it may not bind them strongly so they could be released back in to the water and sediment (Crannell, 2007). This allows contamination to persist because the contaminants are not permanently bound and microbial activity can foul and destroy the activated carbon.

Recently a phosphate rock used for reactive capping on land has started to be used for the same purpose in water. This material, black apatite, a by–product of phosphate mining, is a naturally occurring, sedimentary rock that is also used in fertilizer (Crannell, 2007). Black apatite reacts with metals and not only adsorbs but retains them in its crystalline structure, thus making a safe and easily disposable end product.

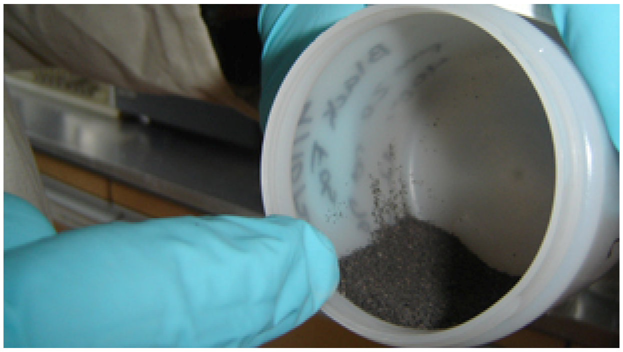
Studies done with apatite in its natural state have shown it to be a very good adsorption material of some metals, but not others. Previous studies have also shown that grinding the stone increases its adsorption properties (Crannell, 2007). But while apatite works well on metals, it does not work on organic compounds. Most heavily contaminated sites contain a combination of metal and organic pollutants; therefore both need to be treated at the same time and preferably by the same method. In an attempt to find this method, I tried to combine the adsorptive capabilities of apatite and activated carbon into one treatment method.

A Hunger for Results

Apatite comes in a variety of forms but is most often a sandy grey color with a low carbon content. The raw material I used was a black apatite rock with relatively high carbon content. The black color is indicative of higher carbon levels. Bradley Crannell collected the raw material from a phosphate mining operation in North Carolina. One of the advantages of using black apatite is that it is a by–product of mining and therefore a free, recyclable material.

The author points to small pieces of black apatite he had to sort out from the raw material.

I started by sorting out the black apatite rocks from the other apatite sediments and grinding them down to a specific size (20 mesh to 70 mesh, or 1 mm to 0.2 mm). I then activated the ground apatite using heat along with water, air, and/or nitrogen. I determined the best activation method by trying these different methods and then testing the activated materials' abilities to adsorb zinc and arsenic. I discovered that the best activation method was heating the rock to 400°C in a nitrogen atmosphere. The heat and the inert nitrogen atmosphere with no oxygen present changed the chemistry of the apatite's surface, allowing it to more easily adsorb the contaminants.



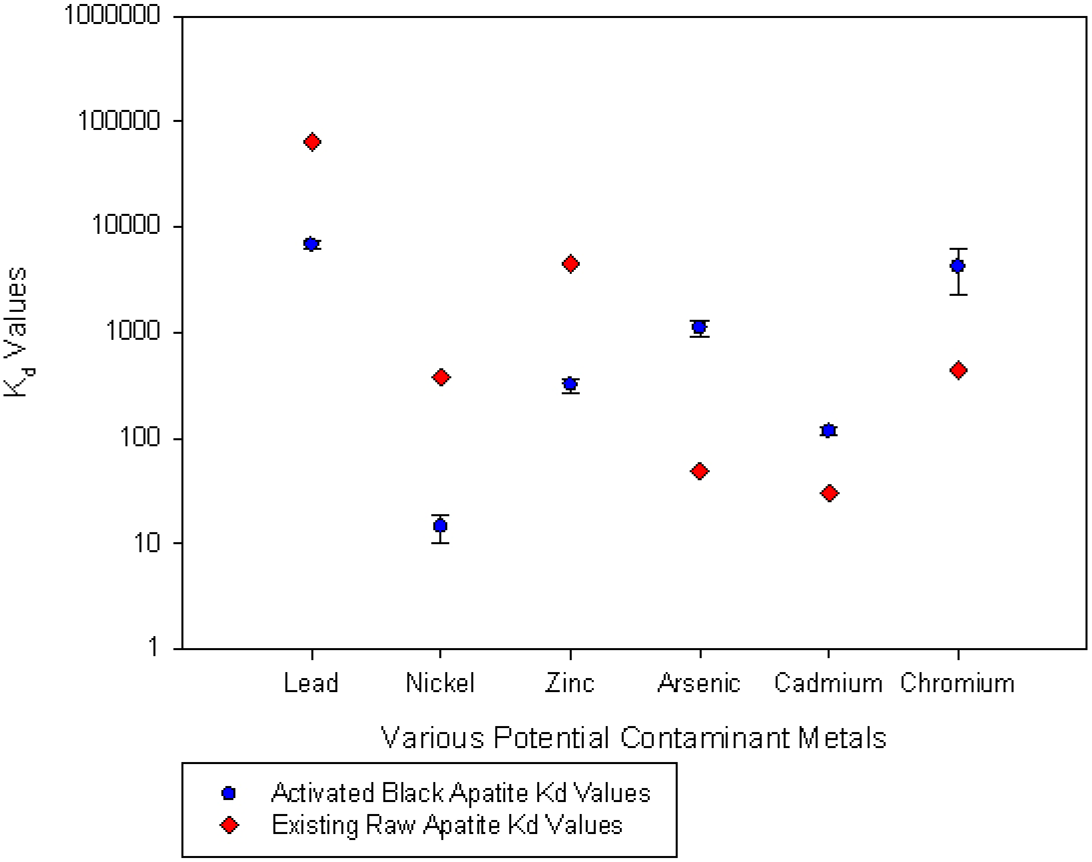
After being separated from other types of apatite, the black apatite was ground into a fine dust.

To test the adsorption capabilities of the activated black apatite, I performed batch studies by adding apatite to a synthetic water source with different metal and organic contaminants and mixing them for three days on a rotary mixer. Afterward I skimmed water off the top of each sample and analyzed it for contaminant concentrations. The difference between the amount of contaminant present in the water at the beginning and end of the trial equals the amount of contaminant that the apatite was able to adsorb.

I compared adsorption rates of activated apatite versus raw apatite using K_d values. K_d values are determined by taking the amount of the contaminant adsorbed and dividing it by the amount of the contaminant remaining in solution. This means that the higher the value, the better the material did at adsorbing the contaminant. K_d values are useful because they can be compared regardless of the initial concentration of the contaminant in solution or the amount of adsorbent used.

As can be seen in Figure 1, activated apatite adsorbed much more of some metals than the raw apatite did, while it actually adsorbed less of other metals. The values for raw apatite were not generated through my research but taken from an existing study done by the US Department of Energy (Bostick, 2003).

Figure 1: The K_d Values of Various Metals that Could be Potential Contaminants in Sediment



My results also showed that the activated black apatite adsorbed some of the organic contaminants. This is significant because raw apatite doesn't have the same organic adsorption capabilities. The activated black apatite appeared to work better on lower concentrations of contaminants but still had some effect at higher contamination levels. This is especially good news for contaminated sites that contain organics because my results show that activated black apatite will be more effective than raw apatite in cleaning up sites containing both organics and heavy metals.

To summarize, I found that activated black apatite compared to raw apatite works better on some metals, worse on others, and does work on a smaller scale for organic remediation. This doesn't mean, however, that activated apatite is better than raw apatite; it means that both apatites should be used for situations with different contamination issues. For instance, if there is a river bed containing chromium, arsenic, and PCBs or PAHs, the activated black apatite will work much better at cleaning the soil and trapping all of the pollutants. On the other hand, if there is a lake bottom with high lead and zinc concentrations, then raw apatite will perform best on the contaminants.

Completely Full: No Apatite Left

Although the results were not what I was hoping for and I did not discover a material that effectively adsorbs all metals and organics, this project helped me gain tremendous insight into *in–situ* sediment remediation. It also has practical implications. Activated black apatite has not yet been used for real–world remediation, but could be if the right situation presented itself, such as for treatment of sites containing the specific metals or organics that black apatite adsorbs.

The research I conducted showed me an entire new world outside of academia. I had to take things like economics and real world applicability into account to ensure I was making a useful product. This wasn't just research for the sake of knowledge; this was *real* research and development. As I continue with my bachelor's in environmental engineering and eventually pursue my master's in civil engineering with a concentration in environmental engineering, I am not certain whether I will continue with remediation issues. However, I certainly will continue to conduct research and apply the invaluable skills I gained from this experience.

I would like to thank my mentors, Mr. Bradley Crannell and Dr. Jeffery Melton. Without their constant guidance and infinite wisdom into the world of apatite, this project would never have been possible. I would also like to thank Bhawana Sharma, for without her analytical expertise and help there would be no data, just thousands of random, meaningless numbers.

References

Bostick, William D.; Stevenson, R.J.; Harris, L.A.; Peery, D.; Hall, J.R.; Shoemaker, J.L.; Jarabek, R.J.; Munday, E.B. "Use of Apatite for Chemical Stabilization of Ubsurface Contaminants." Materials and Chemistry Laboratory, Inc. US Department of Energy, Contract DE–AC26–01NT41306. (2003) 1–186.

Brodkin, Elizabeth; Copes, Ray; Mattman, Andre; Kennedy, James; Kling, Rakel; Yassi, Annalee. "Lead and Mercury Exposures: Interpretation and Action." CMAJ: Canadian Medical Association Journal. 176 (2007) 59–73.

Carpenter, David O.; Arcaro, Kathleen; Spink, David C. "Understanding the Human Health Effects of Chemical Mixtures." Environmental Health Perspectives. 10 (2002) 25–42.

Crannell, Bradley. Personal Interviews. 2005–2007.

Gonzalez, P; Zaror, C; Carrasco, V; Mondaca, M A; Mansilla, H. "Combined Physical–Chemical and Biological Treatment of Poorly Biodegraded Industrial Effluents." Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances & Environmental Engineering. A38 (2003) 2201–2208.

Phelps, Jerry. "Prenatal PAH Exposure Causes Genetic Changes in Newborns." Environmental Health Perspectives. Volume 113, Number 4, April 2005.

Author Bio

An environmental engineering major from Nottingham, New Hampshire, ***Owen Friend–Gray*** *has been conducting research under the guidance of Dr. Jeffrey Melton since his freshman year. In spring 2007 Owen received an Undergraduate Research Award (URA), which allowed him to continue his studies on environmental contaminant remediation. "I learned that research doesn't always go the way you want, [but] there are no right and wrong answers," Owen says. "The results are what they are." Owen intends to graduate in December 2008 and immediately begin work on his master's degree. With that and his future career plans as an environmental engineer in mind, he submitted this article to Inquiry so that he could learn how to reach a broader audience. After all, "most of a scientist's audience is typically, in the end, non–scientists," remarked Owen.*

Mentor Bio

Jeffrey S. Melton *is a research assistant professor in the Department of Civil Engineering, who specializes in remediation of contaminated soil and sediment and in recycling materials such as crushed concrete into construction projects. As a member of the Environmental Research Group, Dr. Melton has been conducting research on the use of phosphate minerals to remediate sediment contaminated with heavy metals, which ties in closely with Friend–Gray's research. "I didn't know Owen before I asked him to work on the project," admits Dr. Melton. "But it turns out that Owen is a very talented young man, and getting to know him better has been a benefit of this project. The results were interesting but not applicable to sediment remediation, which is fine because now we know that it won't work and that is more than we knew before." Having served as a mentor before, Dr. Melton says that he enjoys interacting with students outside the classroom. "I think the experience makes me a better professor and mentor."*