

Remediation and Beneficial Reuse of Contaminated Sediments

Editors

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SEDIMENT DECONTAMINATION: EVOLUTION AND PRACTICAL APPLICATION OF BIOGENESIS^K WASHING TECHNOLOGY

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ABSTRACT: Research into the removal of organic and inorganic contaminants from soil and sediment, and the practical application of this research in field operations, has been in progress since 1991. The results described in this paper are the foundation of the BioGenesis^K technical approach which uses both chemical and physical means to separate contaminated biomass from inorganic solids and then to clean the solids. Based on the results and subsequent bench and pilot testing, specialized equipment was developed to implement the washing process. At present, the decontamination washing process is being implemented in New York/New Jersey harbor with a capacity of 250,000 cubic yards per year (191,000 cubic meters per year).

INTRODUCTION

Soil washing is an ancient technology, and has been practiced in the mineral extraction industry for centuries. More recently, attrition scrubbing techniques have been used in Europe for treatment of soils consisting of gravel and sand which contain both organic and inorganic contaminants. However widespread application of washing technology has been limited by certain factors illustrated by the following excerpts from government sponsored technology assessments:

- *Fine soil particles (silts, clays) are difficult to remove from washing fluid.*
- *Complex waste mixtures (e.g. metals with organics) make formulating washing fluid difficult.*
- *High humic content in soil inhibits desorption (U.S. EPA, 1993, Remediation Technologies Screening Matrix and Reference Guide).*

and:

Unit processes have proven excellent for media such as sand and gravel, but need to be improved for fine-grained soils where more than 30-35% of particles are less than 0.063 mm (NATO/CCMS, 1998).

BioGenesis constructed its first soil washing gondola in 1991, entered the U.S. EPA's Superfund Innovative Technology Evaluation (SITE) program, and demonstrated soil washing technology during 1992 on 3,800 tons of soil at an oil refinery site in Minnesota (U.S. EPA, 1993, *BioGenesis^K Soil Washing Technology*). During plant operation, both the smaller grain sizes of silt and clay, about 11% of the total, and the more heavily weathered oil contaminated particles, were not cleaned as efficiently as the larger particles of sandy soil greater than 0.063 mm in size. Subsequently, BioGenesis sought ways to improve treatment of small

particles, and working with Environment Canada, bench tested a new washing technique. The new approach is believed to be the first use of washing to effectively decontaminate fine grained silt and clay sediments contaminated with high levels (4,000 mg/kg) of poly-aromatic hydrocarbon (PAH) (Wastewater Technology Centre, 1993).

The research, reported for the first time in this paper, is the basis for the subsequent evolution of sediment washing equipment that has been successfully tested at large pilot scale (U.S. EPA Region 2, 1999), and is now being implemented at a full scale of 250,000 cubic yards per year in New York/New Jersey harbor.

Research Approach. In conjunction with the bench testing for Environment Canada, review of the washing literature showed that conventional washing approaches such as attrition scrubbing were less effective as the grain size of material decreased from sand to silt, and from silt to clay. Additionally, published writings indicated that washing efficiency also decreased as organic content of the soil/sediment increased. Missing from the literature, however, were answers to the questions that would allow improved contaminant extraction efficiency with full scale equipment:

1. What are the limitations of solvent extraction on organic contaminants in fine grained soil and sediment?
2. What is the role of biomass in absorbing organic contamination and preventing the contamination from being desorbed through washing?
3. How do inorganic contaminants partition in organic and inorganic solid particles?
4. How does the use of chemicals, impact pressure, and type of impact surface affect removal efficiencies in washing?
5. How fast does inorganic contamination transfer from liquid to solid, and how much contaminant is distributed between the inorganic solid and the organic solid?
6. What can be achieved with chemical extraction, what can be achieved with physical forces, and what is the optimum balance between the two?

Answers to these questions could lead to more effective chemicals and equipment for decontamination. Therefore the experiments in table 1 were performed, with results that will be discussed in turn.

Table 1. Experiment Summary		
Experiment	Name	Purpose of Experiment
1	Solvent extraction of biomass	Evaluate chemical effectiveness in separating biomass from solids of differing soil grain sizes
2-1	Solvent extraction of #6 fuel oil tank bottoms plus biomass	Determine the correlation between TPH reduction and biomass reduction for differing soil grain sizes
2-2	Biomass absorption of TPH from contaminated water	Determine how biomass absorbs TPH from contaminated water for different soil grain sizes

Table 1. Experiment Summary		
Experiment	Name	Purpose of Experiment
3-1	Lead partitioning from water to the solid phase	Determine how lead in water partitions to differing soil grain sizes
3-2	Lead partitioning from water to the solid phase, biomass added	Determine the effect of biomass addition on partitioning of lead in water to differing soil grain sizes
4	Washing variables	Determine the effect of different surfaces, chemicals, and pressures on washing efficiency
5	Partitioning of lead among solid, organic, & water phases	Evaluate the partitioning of lead from the solid phase to the organic and water phases

MATERIALS AND METHODS

Composition of Test Soils. To enhance the reproducibility and repeatability of results, standard soil mixtures were used for all experiments. The soils were made by sieving a commercially available sand mixture into three size fractions. Grains between 2.0 to 0.15 mm were designated as sand; grains between 0.15 to 0.038mm were designated as silt. For the clay mixture, grains less than 0.038 mm were mixed with bentonite clay in a 40% fines - 60% clay ratio. Biomass was standardized through the use of a commercially available humus liquid.

Experiment 1-1, Solvent Extraction of Biomass. To evaluate chemical effectiveness in separating biomass from solids of differing grain sizes, 4% humus

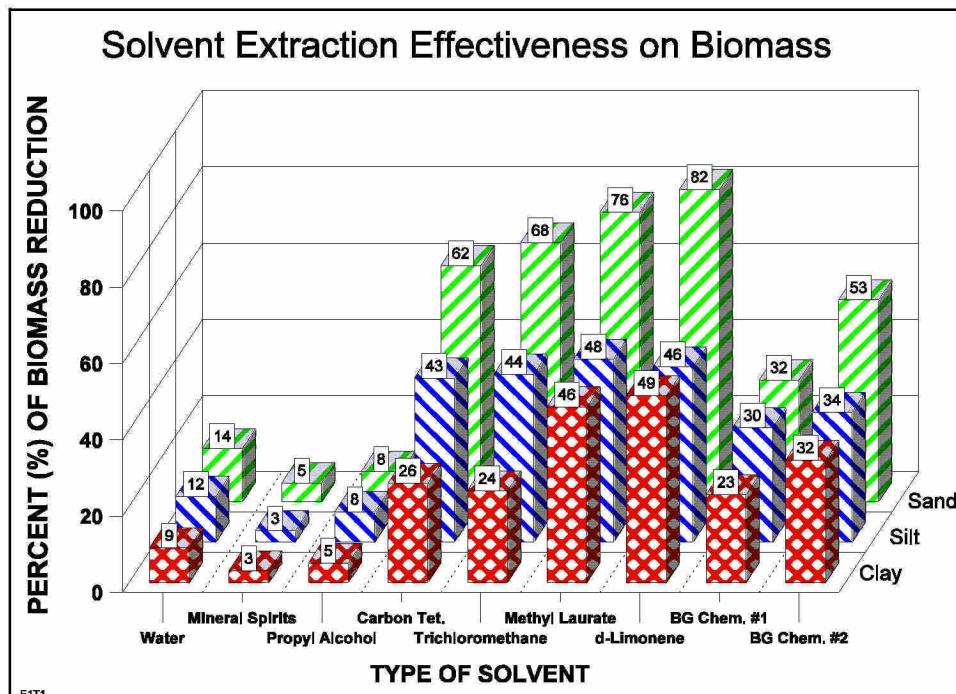


Figure 1. Solvent Extraction Effectiveness on Biomass.

was mixed with 100g each of sand, silt, and clay; mixed well with water; dried; and extracted for 30 minutes with a solvent. The solid phase was dried in a rotoevaporator, burned to remove the organic phase, and weighed before and after burning to determine the amount of organic that remained in the solid phase after the biomass extraction.

Figure 1 shows the results. Water, mineral spirits, and propyl alcohol were ineffective extracting chemicals. Carbon tetrachloride, trichloromethane, methyl laurate, and d-limonene had medium extraction rates with the notable exception that the chlorinated solvents had lower effectiveness on clay. Finally, BioGenesis water-based proprietary surfactant mixtures were competitive with the solvents, but with substantially lower handling hazards. This experiment demonstrated that biomass binds very tightly to silt and clay particles.

Experiment 1-2, Solvent Extraction of #6 Fuel Oil Tank Bottoms Plus Biomass.

To determine the correlation between TPH reduction and biomass reduction for differing soil grain sizes, experiment 1-1 was repeated with the exception that 10% of #6 fuel oil tank bottoms was added to the mixtures. Tank bottoms were selected due to their high concentration of poly-aromatic hydrocarbon (PAH).

Figure 2 shows the results. Within experimental error, the results of the extractions were the same as for experiment 1-1. The result was surprising due to the large amount of TPH. This led to the conclusion that hydrocarbon mixed with biomass becomes an integral part of the biomass phase that binds very tightly to silt and clay particles

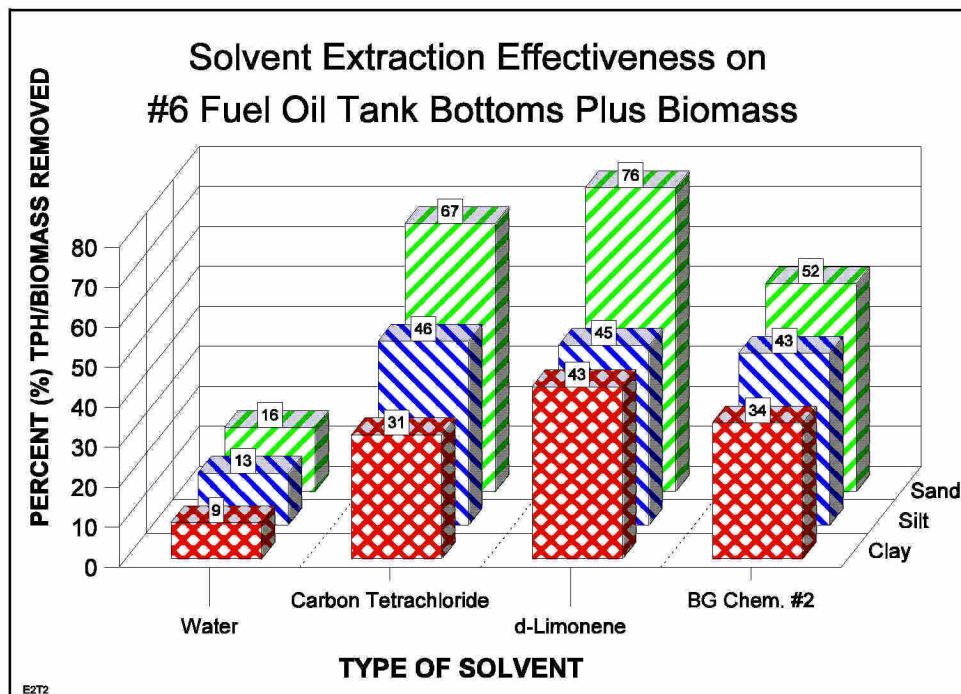


Figure 2. Solvent extraction effectiveness on #6 fuel oil tank bottoms plus biomass

Experiment 2, Biomass Absorption of TPH from Contaminated Water. To determine how biomass absorbs TPH from contaminated water for different soil grain sizes, 4% humus was mixed with 100g each of sand, silt, and clay. To the soil samples was added a mixture of 10% hydrocarbon in water. At 30, 60, 90, and 120 days, samples of the solids were dried in a rotoevaporator, burned at high temperature, and weighed before and after to determine the amount of hydrocarbon that had been absorbed by the sample.

Figure 3 shows the results. The sand, silt, and clay samples each absorbed TPH at a steady rate. However the clay/biomass sample absorbed 2.3 times the amount of TPH absorbed by the sand/biomass sample, and 1.5 times the amount of TPH absorbed by the silt/biomass sample. This illustrates the greater affinity of hydrocarbon for solids/biomass than for water.

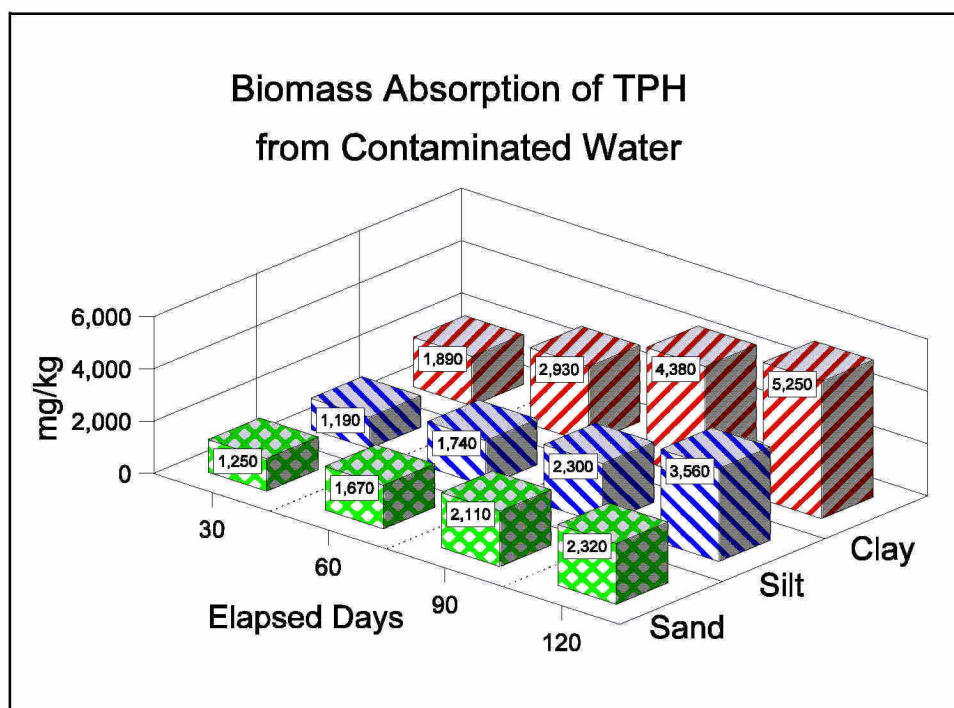


Figure 3. Biomass Absorption of TPH from Contaminated Water.

Experiment 3-1, Lead Partitioning from Water to the Solid Phase. To determine how lead in water partitions to differing soil grain sizes, a mixture of water containing 5,000 mg/kg lead nitrate was mixed with 100g each of sand, silt, and clay. At 15, 30, 60, 90, 120, and 180 days, the samples were mixed, and the lead content of the water phase was determined.

Figure 4 shows the results. The lead remaining in the water phase decreased gradually, and the clay and silt fractions exhibited the same general behavior in absorbing lead as was shown in figure 3 for TPH, though the absorbency differences between clay, silt, and sand were not as large.

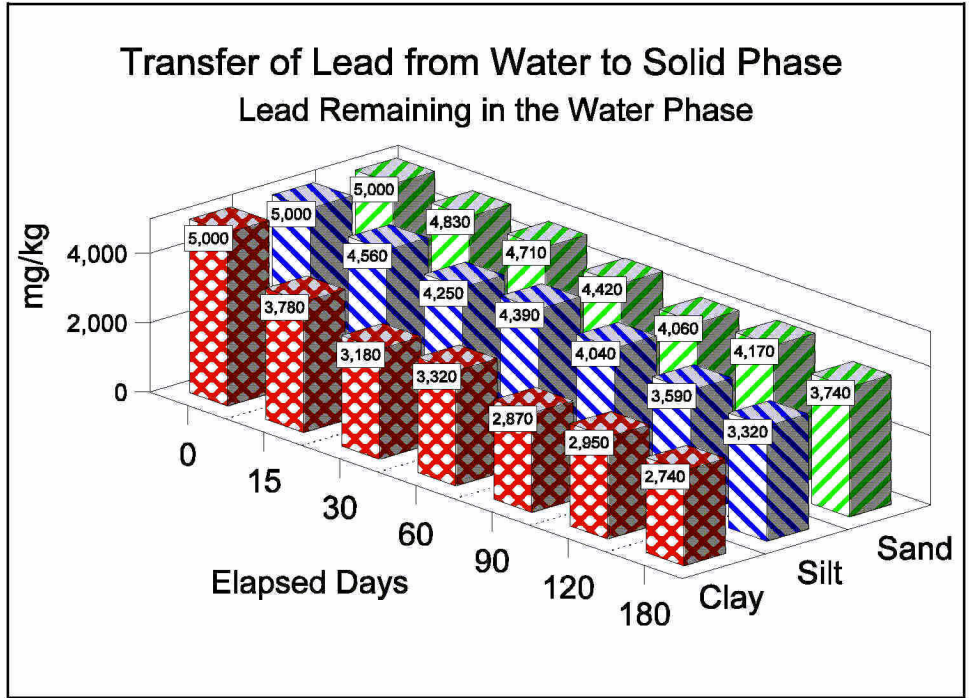


Figure 4. Transfer of Lead from Water to Solid Phase.

Experiment 3-2, Lead Transfer from Water to the Solid Phase, Biomass Added
To isolate the effect of biomass addition on partitioning of lead in water to differing soil grain sizes, experiment 3-1 was repeated with one difference. On the 15th day, 2% biomass was mixed with each sample.

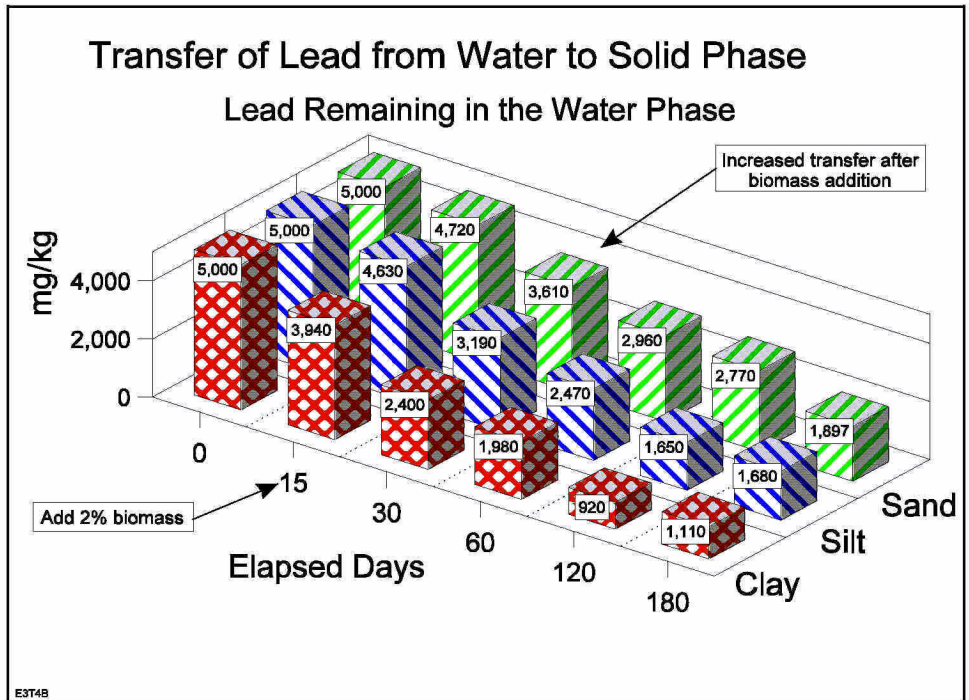


Figure 5. Transfer of lead from water to biomass/solid phase.

The results are shown in figure 5. Absorption of lead at day 15 was about the same as in experiment 3-1. However after biomass was added at day 15, the absorption rate increased to day 30, and then continued at a higher rate than in experiment 3-1. The conclusion is that biomass not only shows strong affinity for organic contaminants (experiment 2), but also for inorganic contaminants.

Experiment 4, Washing Variables. To explore the effect of different surfaces, chemicals, and pressures on washing efficiency, 2.5 mm (1 inch) tubes of aluminum, copper, carbon steel, and stainless steel, each 1.8 m (6 feet) long were filled with irregularly shaped pieces of the same material as the tube. The reason for filling the tubes was to provide multiple scrubbing surfaces in each tube for the sediment slurry to be pumped over. Two slurry mixtures were then prepared consisting of 5% silt, 5% clay, and 90% water. Both mixtures were contaminated with 5,000 mg/kg lead. One of the slurry mixtures also had 2% BioGenesis™ washing chemical added. Then both slurry mixtures were pumped through each of the four types of tubes at pressures of 3.4, 6.8, 34, and 68 bar (50, 100, 500, and 1,000 psi respectively).

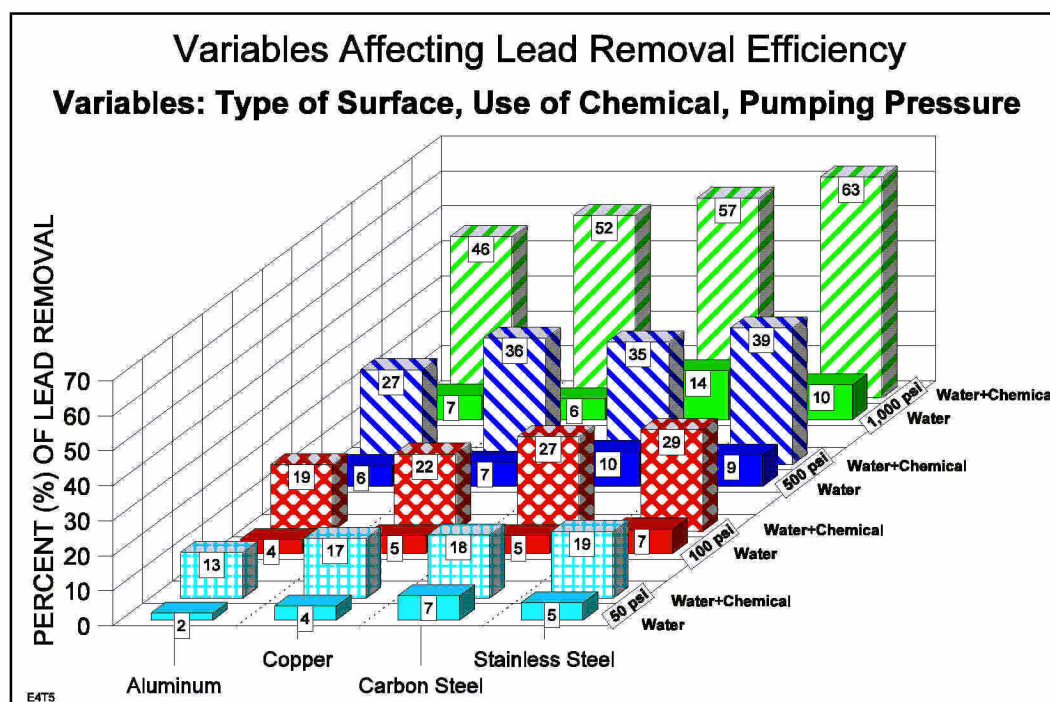


Figure 6. Variables Affecting Lead Removal Efficiency

Figure 6 shows the results. For all cases, use of chemical was clearly superior to water alone by factors of 200% to as much as 700%. In all cases, higher pressures were better at desorbing lead than lower pressures. In the washing chemical experiments, the largest gain in efficiency occurred when pressure was increased from 34 bar (500 psi) to 68 bar (1,000 psi). Assessing the impact of different metals was not conclusive because of experimental conditions where the size, distribution, and position of metal shapes in the tubes could not be controlled. Nonetheless,

washing effectiveness apparently increased somewhat as the hardness of the metal tube increased. Additional research was not undertaken on this factor because stainless steel was already the clear choice for manufacturing equipment for durability reasons.

Experiment 5, Partitioning of Lead among Solid, Organic, & Water Phases. To evaluate the partitioning of lead from the solid phase to the organic and water phases, a mixture consisting of 30% sand, 30% silt, 40% clay, and 0.1% humus was prepared. To the mixture was added 5,000 mg/kg lead nitrate in water. Mixing was done very slowly in order minimize transfer due too mixing as a factor in the experiment. At 10, 20, 30, 60, 90, 120, 150, and 180 days, samples were taken, solvent extracted, and the extract tested for lead content. Aliquots of each sample were also analyzed to determine the lead content remaining in the soil mixture. The soil samples were then dried in a rotoevaporator, burned to remove the organics, and weighed before and after burning.

Figure 7 shows the results. Assuming the partitioning of lead throughout the organic phase of the solid is uniform (this is not proven), the increase in lead content of the organic part of the mixture and the decrease in lead content of the solid part of the mixture combined with little or no change in the lead content of the water phase, all support the hypothesis of inorganic contaminants partitioning to, and being stable, in the organic phase of sediments.

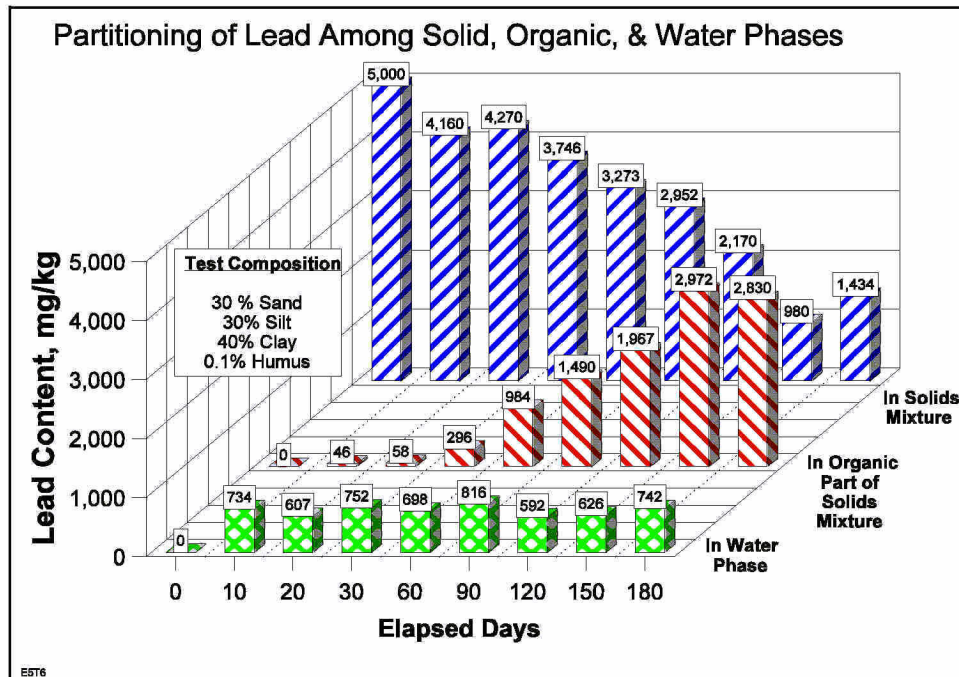


Figure 7. Partitioning of Lead Among Solid, Organic, and Water Phases.

IMPLICATIONS FOR FULL-SCALE SEDIMENT WASHING OPERATIONS

Table 2 summarizes the results of the experiments, their conclusions, and the practical implications for washing technology development.

Table 2. Experimental background for development of BioGenesisK Washing Technology			
Experiment	Name	Conclusion	Conclusion: Practical Implication for Washing
1-1	Solvent extraction of Biomass	Biomass is strongly bound to silt/clay particles	If contaminants are in the biomass, chemical alone cannot clean completely
1-2	Solvent extraction of TPH & Biomass	Hydrocarbon mixed with biomass becomes an integral part of the biomass phase	Chemicals alone cannot clean completely
2	Biomass absorption of TPH from contaminated water	Hydrocarbon has more affinity for biomass and solids than for water	Should focus on separating the organic phase from solids
3-1	Partitioning of lead in the water phase	Lead partitions gradually to the solid over time; somewhat faster to smaller particles	Expect more contamination in smaller particles
3-2	Partitioning of lead to the organic/solid phase	Lead partitions much faster and more completely in the presence of biomass	Should focus on separating the organic phase from solids
4	Variables affecting removal efficiency	Chemicals and higher pressures enhance scrubbing effectiveness	Use chemicals at as high a pressure as possible
5	Solvent extraction of biomass	Lead partitions strongly to the organic phase	Should focus on separating the organic phase from solids

From the basic experiments described in this paper, BioGenesis evolved the concept of combining tailored chemicals with specialized sediment washing equipment that would result in desorbing contaminants and biomass containing contaminants from inorganic solids into the water phase. This concept is summarized in table 3, with the specialized equipment implementing the physical means and their purpose illustrated in figures 8, 9, and 10.

Table 3. BioGenesisK Washing Concept		
Means Employed	Extract Contaminants Using	Destroy Contaminants Using
Chemical Means	<ul style="list-style-type: none"> • Tailored Washing Chemicals 	<ul style="list-style-type: none"> • Chemical Oxidation • Chemical Degeneration
Physical Means	<ul style="list-style-type: none"> • Preprocessor Equipment • Collision Chamber 	<ul style="list-style-type: none"> • Cavitation

The BioGenesisK Sediment Preprocessor uses water at 680 bar (10,000 psi) pressure to fractionate sediments and separate biomass from inorganic solids. It processes 800 liters per minute (200 gpm) of a 35% sediment slurry.

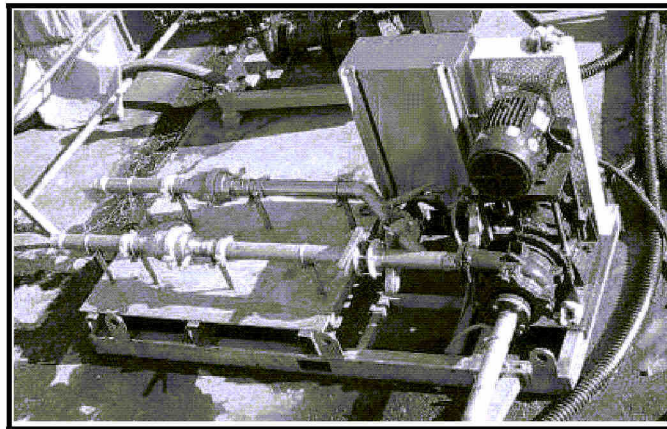


Figure 8. BioGenesisK sediment preprocessor.

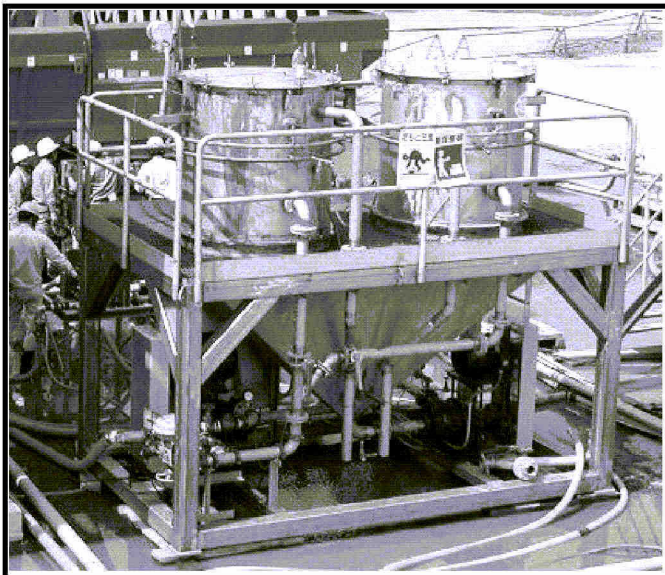


Figure 9. BioGenesisK Collision Chamber.

The BioGenesisK Collision Chamber uses water at 680 bar (10,000 psi) pressure to desorb contaminants from inorganic solid sediment particles. It processes 800 liters per minute (200 gpm) of a 35% sediment slurry, using one processing head. A second processing head is provided for use while the other is in maintenance.

The BioGenesisK Cavitation Unit uses induced cavitation and hydrogen peroxide to destroy organic contaminants. It processes slurry or water at rates of from 200 to 2,000 liters per minute (50 to 500 gpm) depending on the contaminant and its concentration in the slurry or water.

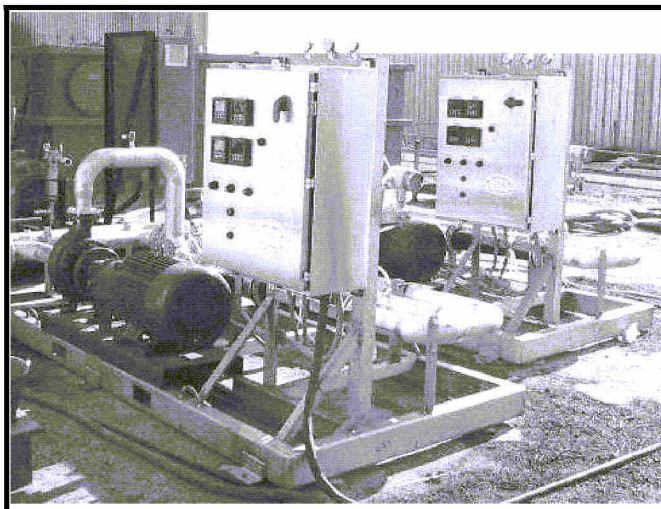


Figure 10. BioGenesisK Cavitation Unit.

CONCLUSION

This paper has described the experimental basis for BioGenesisK Washing Technology, and has shown how experimental results led to the development of specialized sediment processing equipment. Decontamination of sediments using washing technology is still an infant industry. However, BioGenesis has demonstrated that the decontamination of sediment is possible. All the results are promising and show that the washing process can be commercially viable. As commercial plants become more numerous and more practical operational data is obtained, the whole process can be optimized for different regions and contaminants.

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