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Permeable reactive barrier using atomized slag material for treatment of contaminants from landfills

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ABSTRACT: This paper presented a permeable reactive barrier using atomized slag material for the treatment of landfill leachate and contaminated ground water. This study investigated the feasibility of using atomized slag and modified byproducts from iron and steel making industries as new reactive material for leachate treatment. Batch and column tests, and field pilot tests were performed as model systems to explore the effect of atomized slag as an alternative reactive material. From the evaluation of various atomized slag based PRB systems, a combination of an atomized slag and sand system was found to have a substantial reaction capacity for leachate and organics, thus it has the potential to be used in the permeable reactive barriers for a subsurface remediation. The test results showed that the adsorption capacity is high in the order of pH 7 > pH 5 > pH 9, the heavy metal removal rate is high in the order of Cd > Pb > Cr > Cu, and organic removal rate is high in the order of T-P > COD > T-N.

Key words: atomized slag, reaction, permeable reactive barrier, treatment, contamination

1. INTRODUCTION

Permeable reactive barrier (PRB) is a passive in-situ treatment technology that uses natural groundwater flow conditions of a site for remediation as shown in Figure 1. Methods of PRB installation include constructing a trench across the contaminated groundwater flow path by using either a funnel-and-gate system or a continuous reactive barrier. The gate or reactive cell portion is filled with a treatment media of typically zero-valent granular iron, which is derived from treated scrap metal to remove its valence electrons (Henry et al., 2003; Hunter, 2002; Robertson et al., 1995, 1999). The iron filings react with the target contaminants in a strong reducing reaction to form non-toxic, easily biodegradable, by-products, such as ferrous iron, chloride, hydroxide ions, and light hydrocarbon compounds.

In recent years, zeolite and zero-valent irons have been widely studied to treat organics (Orth et al., 1996; Roberts et al., 1996). Numerous laboratory and filed experiments have been reported on the use of zeolite and zero-valent irons to degrade leachate and organics in permeable reactive barriers (O'Hannesin et al., 1998). Although zeolite and zero-valent iron yielded a very rapid purification of leachate and organics, it may be too expensive to be used commercially (US EPA, 1998; Ritter et al., 2002).

Slag is a residual waste product of steel manufacture. It is estimated that the steel slag generated in Korea will increase to 600 million tons per year (Lee, 1998). Landfilling is generally the disposal solution used for this by-product. Recycling slag could provide an excellent means to deal with not only the economic, but the environmental concerns produced by slag disposal issues. This study aims to evaluate the effectiveness of recycled steel slag as an alternative reactive material. The steel slag used for this study is produced by an atomizing method patented worldwide.

The atomized slag, called PS Ball, is a product cut off converter slag generated by the atomizing method. The atomized slag and conventional converter slag are similar in their composite nature in the converter; however, compounds of the composite differentiate themselves because of the different methods of slag treatment. Conventional slag is cooled slowly in an open yard and contains composites of CaO, FeO, Fe_2O_3, and others. Atomized slag is air blowed and cooled rapidly in an open yard and contains composites of CaO, FeO, Fe_2O_3, SiO_2, and others. Currently, sub-4 mm atomized slag is being produced for filter media, ceramic filters, coagulate, construction materials, abrasives, and desulfurizing agents (Ecomaister, 2003).

Atomized slag is a products cut off converter slag generated by the slag atomizing technology (SAT). SAT can produce a valuable product from the waste slag and this products is an environmentally friendly material. The procedure to produce atomized slag is as follows. First, the molten slag generated from the steel making process is collected and the molten slag is atomized and cooled by air The atomized slag is then moved to the sieving machine and classified by size. Figures 2 and 3 show the procedure of atomized slag production from molten slag generated in a steel making plant. In Figure 3, ① is the molten slag, ② is the funnel, ③ is the rapid wind gate, ④ is the cooling water

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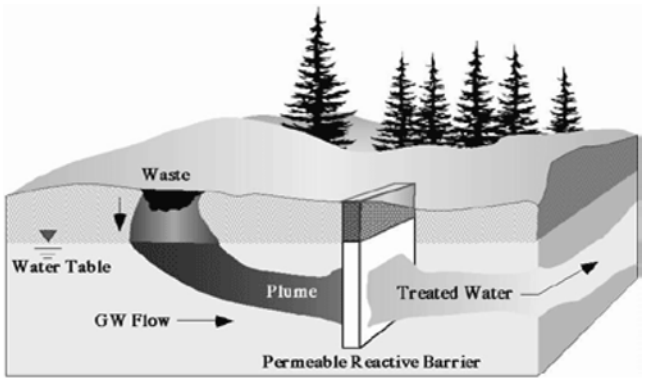


Fig. 1. General permeable reactive barrier system (US EPA, 1998).

system, ⑤ ⑥ ⑦ ⑧ show the sieving, grading, storage, and transportation systems respectively. A comparison of atomiYzed slag and conventional slag is shown in Figure 4.

Conventional slag is used in low grade material and atomized slag is used in high grade material. Atomized slag is reused in water treatment media, filter media, coagulation media, abrasives, desulfurizing agent, and construction material as a alternative sand and fine gravel. The conventional adsorptive and reactive materials are Fe^{o}, Zeolite, others which are expensive products. Hence, an alternative reactive material such as atomized slag was studied in this research. To utilize the atomized slag, the physicochemical property of the atomized slag must be evaluated prior to its use in a permeable reactive barrier. The experimental program of the study included examinations of laboratory batch and column tests, and field pilot tests. Atomized slag was tested for remediating contaminated sites.

Currently, two basic designs are being used in full-scale implementations of permeable reactive barriers, (1) the funnel and gate and (2) the continuous trench. In the funnel and gate system, an impermeable funnel, typically consisting of interlocking sheet pilings or slurry walls, is emplaced to encompass and direct the flow of contaminated water to a gate or gates containing the permeable zone of reactive admixtures of Fe metal and atomized slag. The design must prevent the contaminant plume from flowing around the barrier. Due to directing large amounts of water through a much smaller cross-sectional area of the aquifer, ground water velocities within the barrier will be higher than those resulting from the natural gradient. The continuous trench system is simply a trench that has been excavated and

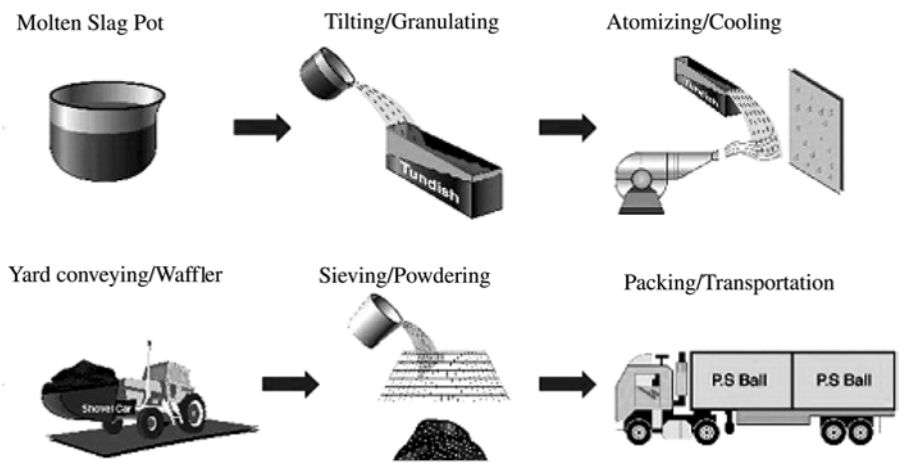


Fig. 2. Procedure of atomized slag production.

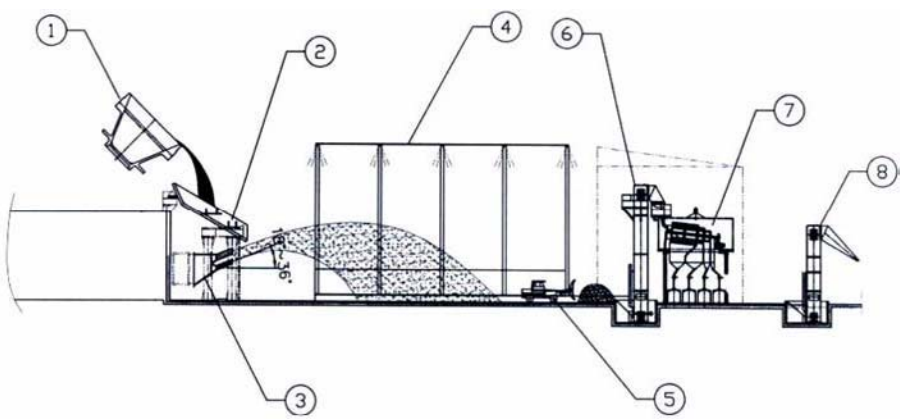
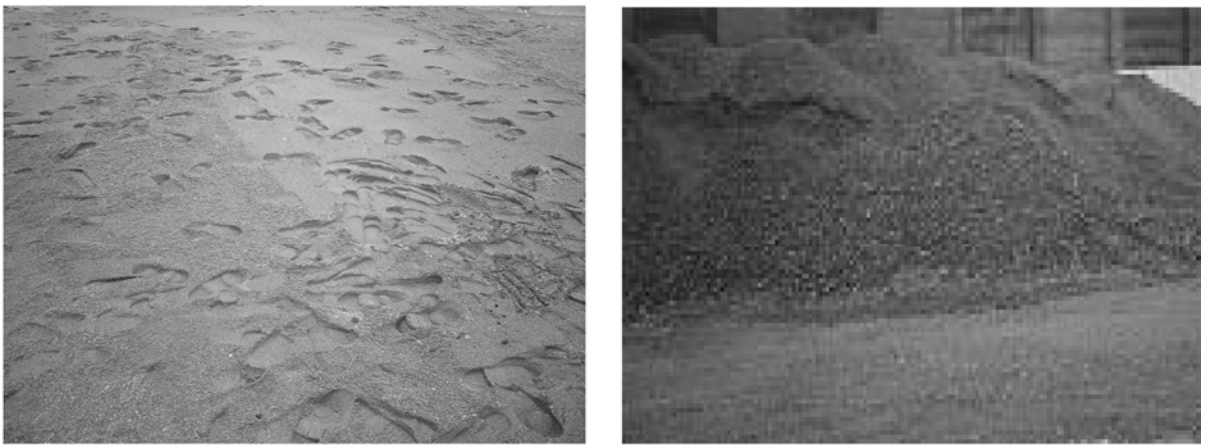


Fig. 3. Detail procedure of atomized slag production.



(a) atomized slag (b) conventional slag

Fig. 4. Atomized slag and conventional slag.

simultaneously backfilled with reactive admixtures of Fe metal and atomized slag, allowing the water to pass through the barrier under its natural gradient.

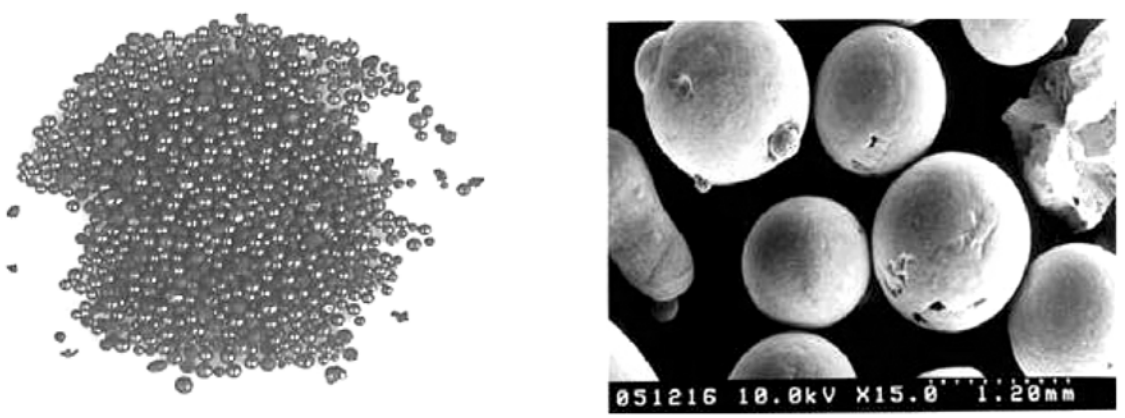
2. MATERIALS AND METHODS

2.1. Sample Preparation

Five types of reactive materials, for use in permeable reactive barriers, were prepared: (1) atomized slag, (2) sand; (3) mixture of atomized slag and sand (8:2); (4) mixture of atomized slag and sand (7:3); and (5) mixture of atomized slag and sand (5:5). Sand is widely available from rivers in Korea and is currently used as a mixture material in permeable reactive barriers; however, it is a relatively expensive material due to high transportation costs. The atomized slag samples were mixed with the sand sample. The mixing ratios of the atomized slag mass to sand mass were 8:2, 7:3, and 5:5 respectively. Atomized slag has sphere grains and are sandy sized, as shown in Figure 5. This material is superior to sand in compressive strength and hardness, and the structure is very stable and safe in terms of physical attack and chemical reaction. This material also has a high weathering and corrosion resistance. Figure 6 illustrates the diagram of filtration and absorption mechanism of atomized slag. Atomized slag has a filtration and adsorption capacity to clean landfill leachates and contaminated groundwaters. The chemicals used were as follows: Pb, Cu, Cd, Cr^{+6} heavy metals in batch test, waste landfill leachate in column test, and contaminated water the in pilot test. The acid solution of 2 N H_2SO_4 and the base solution of 2.5 N KOH were used for pH control in batch test.

2.2. Experimental Program

The gravimetric water content of the samples were measured by weighing the samples before and after drying in an oven for 24 hours at a temperature of 110 °C. The specific



(a) Atomized slag (b) SEM (x 15) picture of atomized slag

Fig. 5. Atomized slag and its SEM picture.

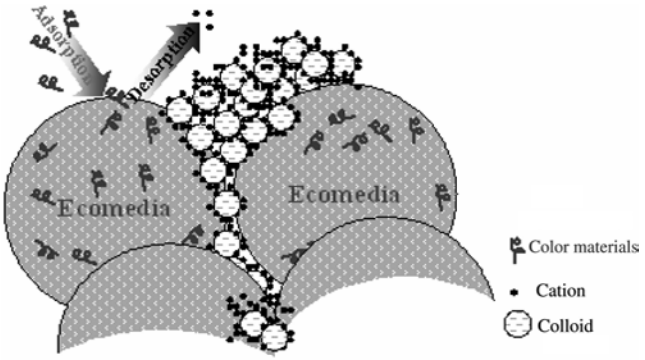


Fig. 6. Diagram of filtration and adsorption mechanism of atomized slag.

gravity of the atomized slag sample was estimated according to the Korean specification method (KS F 2503). Sieve analyses were conducted to investigate the grain size distribution of the slag samples; coefficients of uniformity (D_{10}) and the curvature (D_{60}) of the slag were also calculated. Leaching of heavy metals with pure water was examined with a leaching test designed for the atomized slag samples according to the Korean specification for hazardous wastes. The concentrations of Pb, Cu, As, Hg, Cd, Cr, and CN in the slag sample leachates were measured and compared to the maximum concentration levels of the heavy metals.

The batch test was conducted for heavy metals in an individual 24-ml borosilicate glass vials with triple seals at room temperature that were designed to prevent losses of volatile organic compounds and to minimize the intrusion of oxygen during the experiments. The atomized slag was weighed into the vials and then aliquots of the water, stock solutions, and the acid or base solution were transferred to the vials. The vials were almost completely filled with on aqueous solution to minimize gas phase partitioning of volatile reactants. The initial concentration of Pb, Cu, Cd, and Cr were 50 ml/L, 50 mg/L, 25 mg/L, and 25 mg/L respectively.

The column test was conducted for a real waste landfill leachate sampled from waste landfill site in Korea. The column size is 10 cm in diameter and 60 cm in height, and made with glass material. The pumping rate for applying influent to the column was 0.8 mL/min. The influent was

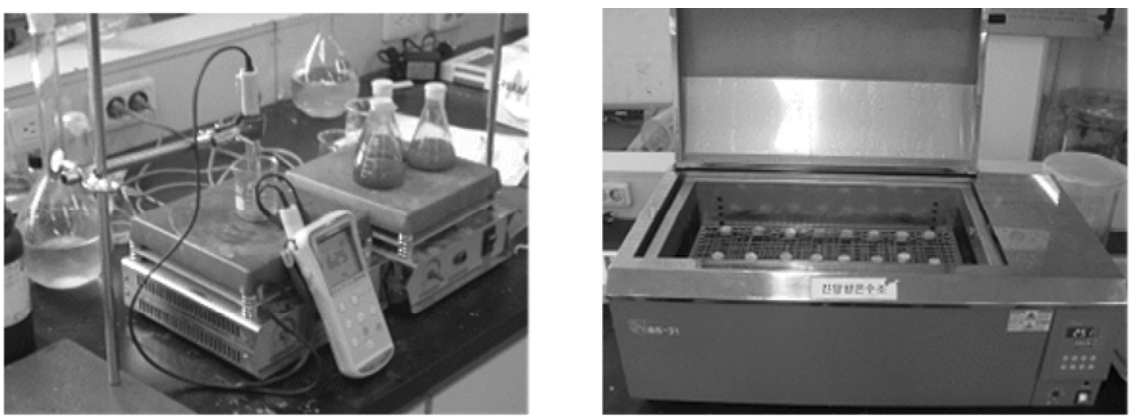


Fig. 7. pH control and batch test set.

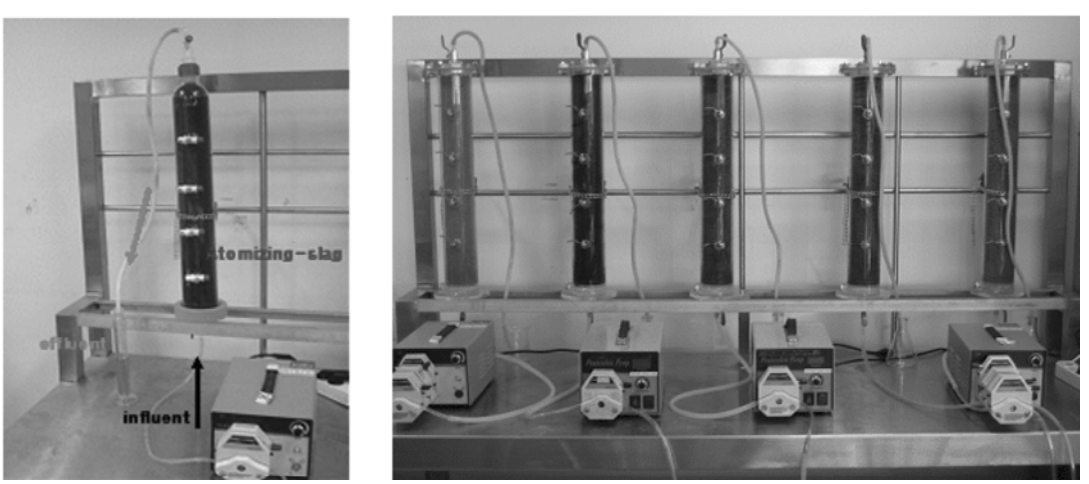


Fig. 8. Column test set.

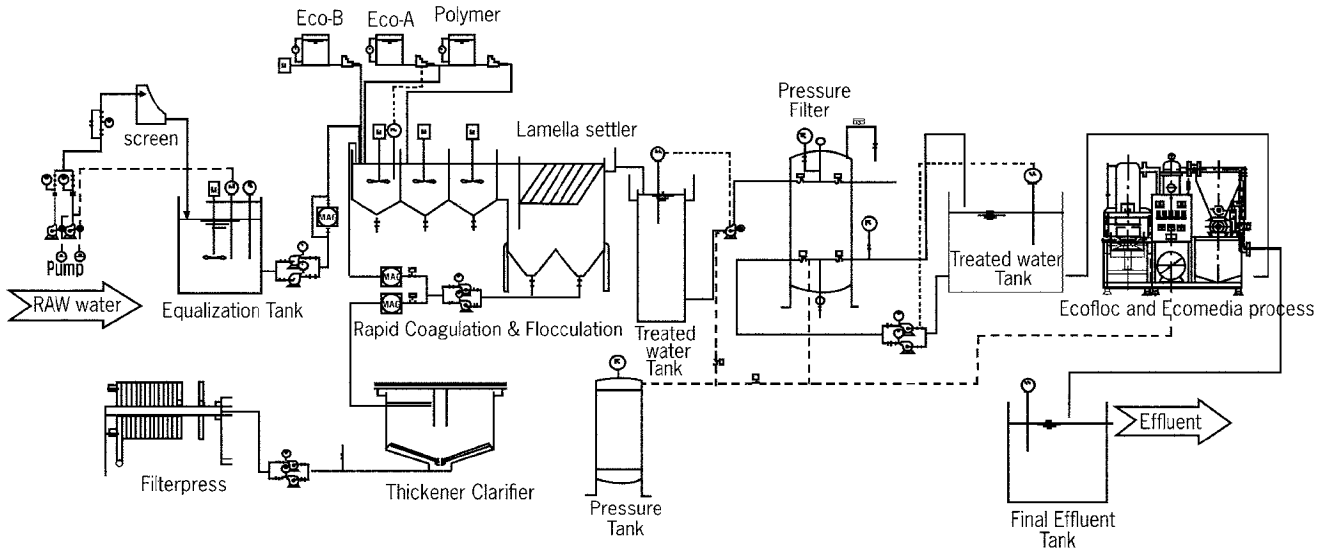


Fig. 9. Schematic diagram of pilot test.

waste landfill leachate and its initial concentration was 642 mg/L of COD 1.8 mg/L of T-P 181 mg/L of T-N. The effluent quantity was checked and collected periodically by a messcylinder and the effluent concentration was measured by chemical analysis.

The pilot test was conducted for real contaminated waste water sampled from a river site in Korea. The pilot test was installed in the field. The pilot test capacity was 300 m^3/day and the pilot test was operated for 11 months in the field. In order to meet the groundwater standard, reactive barrier made of slag material was synthesized and used to polish the effluent from the Ecofloc and the Ecomedia process. The system was automatically operated and its performance was predicted by an analysis model.

3. RESULTS AND DISCUSSION

3.1. Material Property of the Atomized slag

3.1.1. Engineering properties

The measured value of specific gravity was higher than that of typical sand. It was observed that the compressive strength and hardness of the slag were two times higher than that of sand. The abrasiveness ratio of the slag was significantly lower than that of typical sands. The shape of the slag produced by the atomizing process is generally spherical according to the calculated value of uniformity coefficient. The measured water content of the slag ranged from 0.79 to 0.98%. The atomizing is superi or to sand on compressive strength and hardness as seen in Table 1.

Grain size distribution plays a key role in determining the significant engineering properties of coarse materials. According to the grain size distribution analysis measured by a sieve process, the size distribution of sand is between 2.0 mm and 0.075 mm. This means that the sand particle is passing #10 sieve and remaining #200 sieve.

The estimated D_{10} and D_{60} of the atomized slag were 0.43 mm and 1.30 mm, respectively. The calculated coefficient of uniformity and gradation were 3.02 and 1.06 respectively. The grain distribution of the slag samples was good and the size and shape of the samples were uniform, as shown in Table 2.

3.1.2. Chemical leaching

Table 3 shows the chemical constituent of the samples. As shown in Table 3, the atomized slag consists of CaO, Fe_2O_3, and SiO_2. According to the results of the leaching test, the heavy metal concentrations of the slag leachate were lower than the maximum concentration level based on Korean standards for hazardous wastes. Table 4 indicates that there was no measurable concentrations of Pb, Cu, As, Hg, Cd, Cr, and CN from the collected leaching liquid samples of atomized slag.

Table 2. Grain size characteristics of atomized slag samples

Sample I.D.	atomized slag
D_{10} (mm)	0.43
D_{60} (mm)	1.30
C_u	3.02
C_g	1.06

Table 1. Properties of atomized slag

Specific gravity	hardness (Hv)	abrasiveness (%)	strength (kg/cm^2)	uniformity	water content (%)
3.54	500–700	0.1	223	1.22	0.79–0.98

Table 3. Chemical constituents of typical atomized slag

Weight (%)	CaO	Fe_2O_3	SiO_2	MgO	FeO	Al_2O_3
atomized slag	14 to 63	22 to 45	10 to 20	6 to 10	<3	<5.5

Table 4. Summary of leaching test

Analyte (unit: ppm)	[a]MCL	atomized slag
Pb	< 3.0	N.D.
Cu	< 3.0	N.D.
As	< 1.5	N.D.
Hg	< 0.005	N.D.
Cd	< 0.3	N.D.
Cr	< 1.5	N.D.
CN	< 1.0	N.D.

[a]MCL refers to maximum concentration level
[b]N.D. denotes no detection

3.2. Batch, Column and Pilot Test

Prior to evaluating the performance of atomized slag-based systems, considerable reactivities were expected in the system containing the atomized slag only because it contains a substantial amount of solid phase Fe(II) in its structure.

Figure 10 shows the batch test results. The concentration of liquid in vials decreased with a time elapse because the absorption capacity and amount of atomized slag increased with time in the system with constant concentration. Pb concentration rate decreased with time and Pb removal rate increased with time. Pb removal rate reache 85% after 50 hrs and 92% after 96 hrs at pH 7, 82% after 50 hrs and 90% after 96 hrs at pH 5, and 70% after 50 hrs and 83% after 96 hrs at pH 9. The Cu concentration rate decreased with time and the Cu removal rate increased with time. The Cu removal rate reached 72% after 50 hrs and 88% after 96 hrs at pH 7, 68% after 50 hrs and 80% after 96 hrs at pH 5, and 50% after 50 hrs and 63% after 96 hrs at pH 9. The Cd concentration rate decreased with time and the Cd removal rate increased with time.

The Cd removal rate reached 93% after 50 hrs and 96% after 96 hrs at pH 7, 79% after 50 hrs and 85% after 96 hrs at pH 5, and 70% after 50 hrs and 78% after 96 hrs at pH 9. The Cr concentration rate decreased with time and the Cr removal rate increased with time. The Cr removal rate reached 76% after 50 hrs and 89% after 96 hrs at pH 7, 58% after 50 hrs and 68% after 96 hrs at pH 5, and 48% after 50 hrs and 60% after 96 hrs at pH 9. The figure also shows that pH dependency is similar in the atomized slag/sand systems. The optimal pH for the atomized slag systems exists at about the neutral pH value of 7.

A decrease in the reactivity is observed in the atomized slag systems when the pH is low (pH=5) or high (pH=9). However, as shown in the pH 7 experiment, the atomized

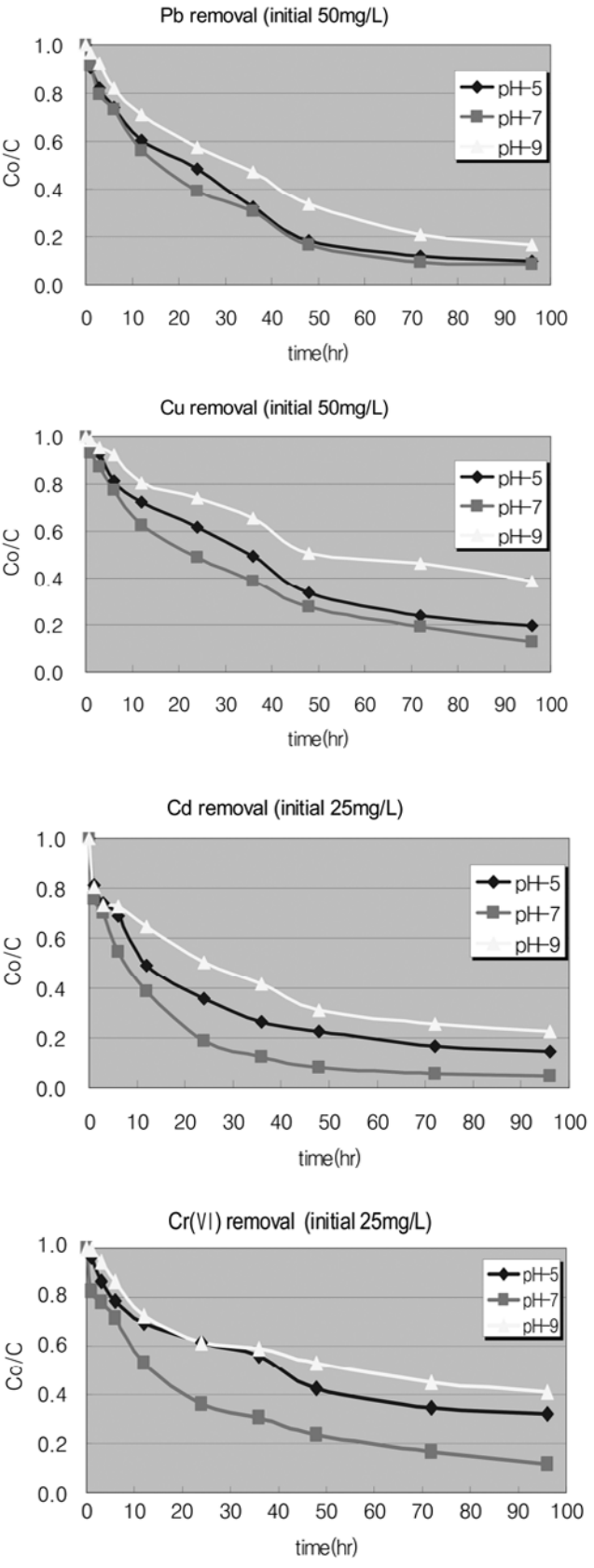


Fig. 10. Batch test results.

slag system still retains at a highest reaction capacity for heavy metal in the neutral pH conditions. From these results, the range of the heavy metal removal rate is 60-95% over the entire tested range, the absorption capacity is the order of pH 7 > pH 5 > pH 9, 80% removal time for pH 7 is Pb 48 hrs, Cu is 96 hrs, Cd is 25 hrs, and Cr is 58 hrs, and the absorption affinity is the order of Cd > Pb > Cr > Cu.

Figure 11 shows the column test results. In this figure it is seen that the concentration of liquid passing through the column increased with an elapse in time or a change in pore volume because the absorption capacity and absorption amount of atomized slag decreased with time in the system with continuously applied contaminant concentration. The concentration of effluent passing through the column increased with time and the contaminant removal rate decreased with time in all cases because the absorption capacity of atomized slag decreased with time. When the atomized slag was 100%, the removal rate reached 40% after 10 pore volumes and 28% after 60 pore volumes for COD, 73% after 10 pore volumes and 52% after 60 pore volumes for T-P, and 50% after 10 pore volumes and 18% after 60 pore volumes for T-N.

When 100% sand was used, the removal rate reached 13% after 10 pore volumes and 3% after 60 pore volumes for COD, 64% after 10 pore volumes and 29% after 60 pore volumes for T-P, and 28% after 10 pore volumes and 9% after 60 pore volumes for T-N. In the case of atomized slag 80% and sand 20%, the removal rate reached 40% after 10 pore volumes and 25% after 60 pore volumes for COD, 73% after 10 pore volumes and 58% after 60 pore volumes for T-P, and 46% after 10 pore volumes and 18% after 60 pore volumes for T-N. In the case of atomized slag 70% and sand 30%, the removal rate reached 40% after 10 pore volumes and 19% after 60 pore volumes for COD, 71% after 10 pore volumes and 49% after 60 pore volumes for T-P, and 40% after 10 pore volumes and 17% after 60 pore volumes for T-N.

In the case of atomized slag 50% and sand 50%, the removal rate reaches 25% after 10 pore volumes and 18% after 60 pore volumes for COD, 70% after 10 pore volumes and 28% after 60 pore volumes for T-P, and 38% after 10 pore volumes and 15% after 60 pore volumes for T-N. The following investigation can be drawn from these results. The orders of removal rate or absorption capacity magnitude are atomized slag only 100+0% highest > admixture of atomizing and sand 80+20% > admixture of atomizing and sand 70+30% > admixture of atomizing and sand 50+50% > sand only 100% lowest. The orders of contaminant treatment by atomized slag admixture are T-P > COD > T-N. The removal rate of COD and T-N is 60-80% in initial stage and 20-40% after 30 pore volumes, and the removal rate of T-P is 70-85% in initial stage and after 50-60% after 30 pore volumes. The range of removal rate is 15-60% in slag admixtures and 2-30% in the sand only system.

Figure 12 shows the pilot test results. In this figure, it is

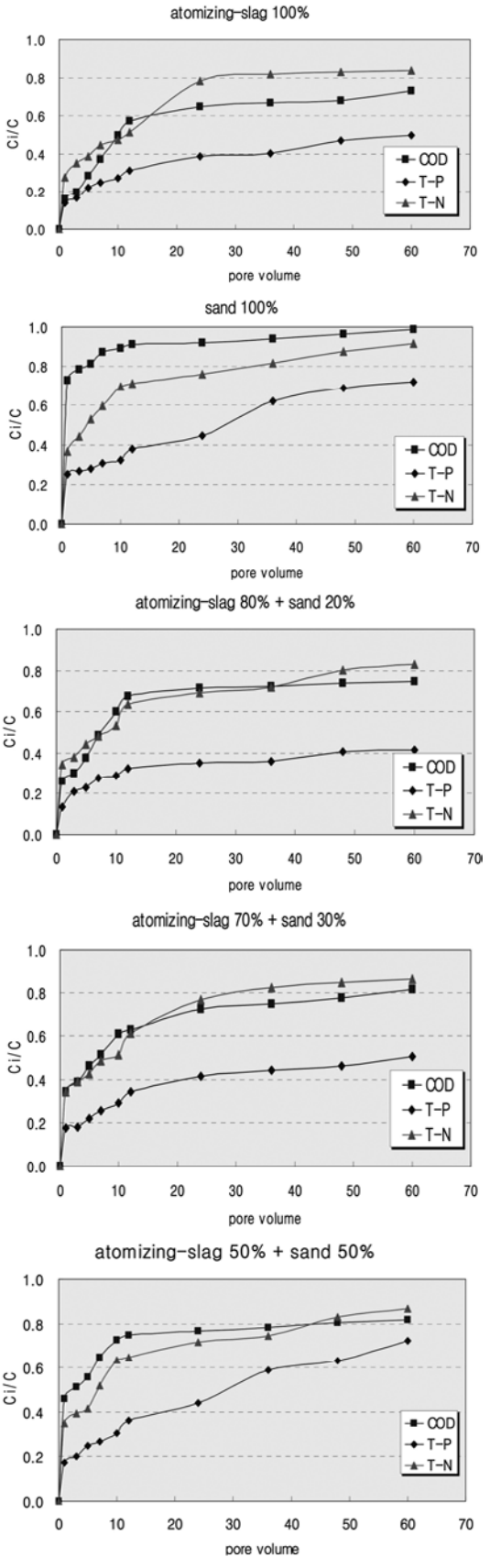


Fig. 11. Column test results.

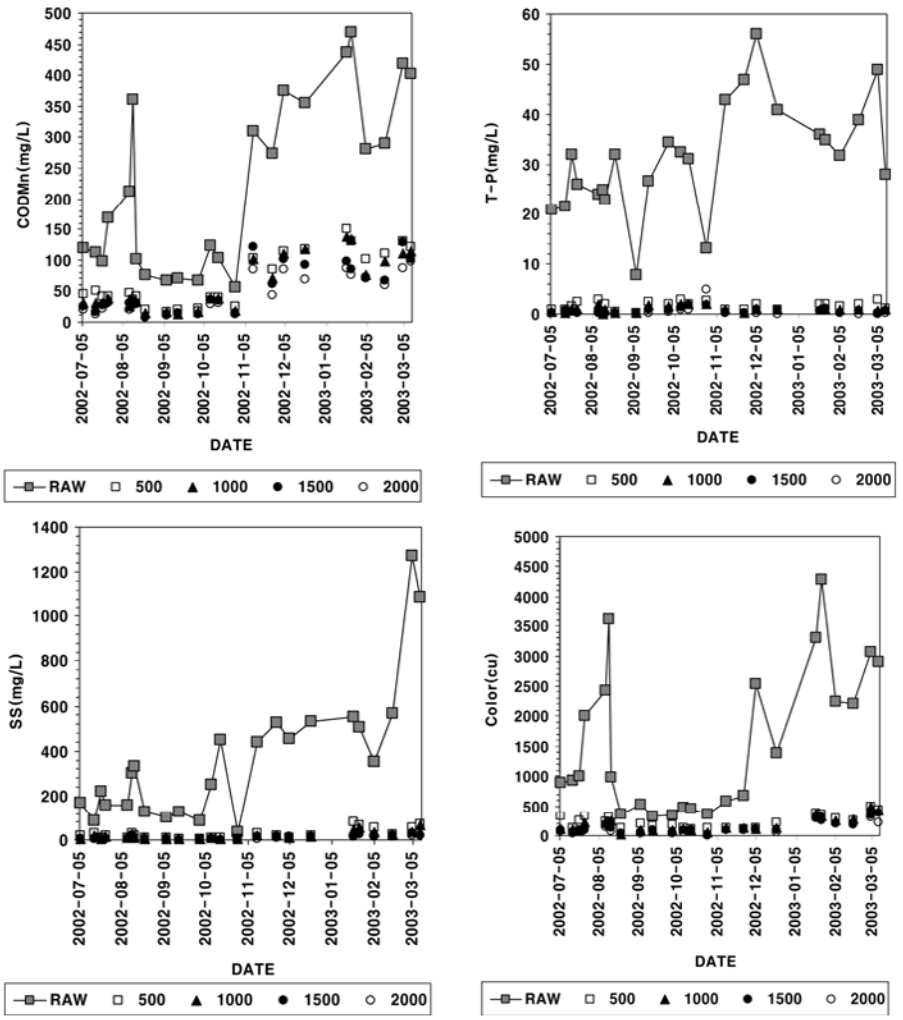


Fig. 12. Pilot test results.

seen that the concentration of liquid passing through the pilot box decreased in any time and season by the effect of the atomizing adsorption capacity. The concentration of effluent COD, SS, T-P, and color significantly decreased compared to the concentration of influent COD, SS, T-P, and color. The decrease of effluent concentration is higher with on increasing input concentration of atomized slag with 500, 1000, 1500, and 2000 mg/L. The pilot test operated for 11 months, even though the influent quality fluctuated during the operation period, the removal rate of COD, SS, T-P, and color were 72.5%, 96.4%, 98.7%, and 92.3%, respectively.

4. CONCLUSION

Based on the results of the evaluation of various atomized slag systems, a combination of atomized slag and sand system was found to have a substantial reaction capacity. Thus it has the potential to be developed into an innovative reactive material that could be placed in permeable reactive barriers used for subsurface remediation.

From the batch test results, the range of heavy metal removal rate is 60-95%, the absorption capacity is as order of pH 7 > pH 5 > pH 9, 80% removal time for pH 7 is Pb 48 hrs, Cu 96 hrs, Cd 25 hrs, and Cr 58 hrs, and absorption affinity is as order of Cd > Pb > Cr > Cu. From the column test results, the orders of removal rate or absorption capacity magnitude are atomized slag only 100+0% highest > admixture of atomizing and sand 80+20% > admixture of atomizing and sand 70+30% > admixture of atomizing and sand 50+50% > sand only 100% lowest., and the orders of contaminant treatment by atomized slag admixture are T-P > COD > T-N. From the pilot test results, the removal rate of COD, SS, T-P, and color were 72.5%, 96.4%, 98.7%, and 92.3%, respectively.

In conclusion, the PRB system with atomized slag is economic because they are made of slag wasted from the steel industies. The system consisting of atomized slag has shown to be effective in removing organics, SS, color, phosphorous, and nitrogen. It is also proved that the system can effectively remove waste landfill leachate and contaminated waste water. Therefore, this technology can be suggested for remediation of contaminated groundwater and landfill leachate.

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