AN INVESTIGATION ON CYANIDE ABSORPTIONPROPERTIES OF SOME INDUSTRIAL CLAYS

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ABSTRACT

Clay minerals have attractive properties due to their ability to absorb some metal and cyanide ions and their major field of application is the ceramic industry. It is well known that several types of clay minerals have been extensively investigated as absorbents in scientific research. In this study; column (static regime) and beaker (dynamic regime) tests were carried out to determine the CN^- ion absorption capacities and to understand the absorption behaviors of clays at different mediums. During the tests, effects of cyanide concentration, pulp density, particle size and contact time on the CN^- ion absorption using two different type clay minerals were investigated. The dynamic tests were done with the ore samples ground to the minus 1 mm size, while the static tests were carried out with samples ground to the minus 0.150 mm which is a typical size fraction utilized at the bottom of tailings dams.

Test results show, 56% absorption for the Bergama clays was obtained at 0.1 g/L NaCN concentration, 30% pulp density at the end of 6 hours mixing time and 0.5 g/L NaCN concentration, 20% pulp density and mixing time of 24 hours with an absorption rate of 76% for The Kireçliköy region sample

INTRODUCTION

Clay type minerals are commonly used as an impermeable layer at the bottom of tailings dams where the CN^- containing tailings of precious metal processes are deposited. It is known that, these clay minerals have low permeability and high ion absorption properties (Atalay, 1997, Fuller, Sparrow, Woodcock 1988). During the interactions between clay minerals and aqua solutions, some ions in the solution are exchanged with the ions located in the lattice structure of clay minerals via absorption (Atalay 1997, Erguvanlı 1995, Yılmaz 1994). The major exchangeable cations of clay minerals are Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+, and Na^+ and anions are SO_4^{2-}, Cl^-, PO_4^{3-} and NO_3^- The reason for ion exchange for illite, chlorite and sepiolite is the tendency to balance electrical charge at silicate and alumina units of the lattice structure and for montmorillonite and vermiculite, the tendency to overcome the electrical charge balance problems occurring as a result of exchange of Al^{3+} and Mg^{2+} at the octahedra layer and exchange of Si^+ and Al^{3+} at the tetrahedra of silicon layer (Yılmaz 1994, Erdinç 1976, EPA 1990, Kara et al. 1998).

The importance of absorption properties of clay minerals comes from the utilization of these clayş as an adsorbent for CN^-containing toxic effluents (Atalay 1997, Kara et al. 1998). The purpose of this study is to determine the CN^- ion absorption properties of different clay minerals at various conditions, therefore to make an approach to CN^- ion capturing capacities of clay minerals.

MATERIALS AND METHODS

Materials

In the experimental studies, two different ore samples were used. The first one was obtained from the Eskişehir-Kireçliköy region, a ceramic quality and cation rich sample and the other one was from the the Bergama region, the clay used at the bottom of the tailings dam of Ovacık gold mine. The particle sizes chosen for the experiments are -1, -0.3, -0.150 and -0.074 mm since the particle size of the clay industrially applied in tailing dams is -1 mm.

The porosity, apparent density and real densities of the clay samples were determined for the evaluation of absorption properties of clays and measurement results for both samples at different size fractions are shown in Table I.

Table I. Porosity and density measurements of clay samples at different size fractions

Sample	Particle size (mm)	Apparent density (g/cm^3)	Real density (g/cm^3)	Porosity (%)
	-1	1.904	2.167	12.1
Bergama	-0.150	1.944	2.189	11.2
Mean Value	-0.038	1.972	2.211	10.8
		1.940	2.189	11.4
	-1	1.745	2.288	23.7
Kireçliköy	-0.150	1.853	2.333	20.6
Mean Value	-0.038	1.889	2.345	19.4
		1.829	2.289	21.2

The results of porosity measurements show that the Kireçliköy sample has much higher porosity indicating that it has more pores available for absorption.

The zeta potential measurements of the clay samples were performed in order to understand the interactions between the ions in the cyanide solution and clay surface The measurable potentials of clay surfaces were found to be negative within the pH range of 9-12. The results of zeta potential measurements are presented in Figure 1.

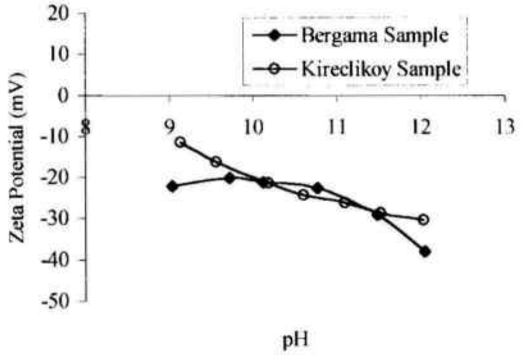

Figure 1. Zeta potentials of the the Bergama and the the Kireçliköy samples as a function of pH.

Specific surface area measurements and fine particle size distribution analyses of clay samples were performed using 'Monosorb' specific surface area analyzer and Malvern particle size analyzer, respectively. Particle size of the samples used for both analyses was below 0.038 mm.

As a result of above mentioned examinations, the Kireçliköy sample was found to have higher specific surface area and lower d_{50} and d_{90} values compared to that of the Bergama sample. The results of specific surface area measurements and d_{50}-d_{90} values are show in Table II.

Table II. Specific surface area measurements and d_{50}-d_{90} values of clay samples.

Sample	Specific Surface Area (m^2/g)	d_{50} (μm)	d_{90} (μm)
Bergama	8.53	15.74	25.11
Kireçliköy	28.38	1.20	4.00

Total chemical analyses of both clay samples were done in order to have idea about the chemical and mineralogical compositions of clay samples. The Bergama sample contains a considerable amount of SiO_2 and Al_2O_3, while the Kireçliköy clay has a relatively higher content of MgO and volatile matter. The results of total chemical analyses can be seen in Table III.

Differential thermal (DTA), thermo gravimetric (TGA) and X-Ray Diffraction analyses methods were followed in the determination of mineralogical composition of clay samples. As a result of mineralogical examinations; quartz, hematite, montmorillonite, kaolinite, kristobalite, muscovite, albite and austite were found in the Bergama sample. Also the Kireçliköy sample can be defined as an illite type clay containing magnesite, saponite, illite, birunite, dolomite and quartz.

Table III. Chemical composition of the Bergama and the Kireçliköy samples.

Element	Bergama Clay (%)	Kireçliköy Clay (%)
SiO_2	61.89	11.57
Al_2O_3	18.13	7.22
TiO_2	0.43	0.62
Fe_2O_3	5.37	1.76
CaO	3.23	2.63
MgO	2.35	33.69
Na_2O	2.10	0.31
K_2O	2.21	0.24
Loss of ignition	4.38	41.4

Methods

Static column and dynamic beaker tests were employed for the determination of cyanide absorption properties of clay samples. Static column test studies were conducted in a column, which was designed to simulate tailings dam structure. At the bottom of the column, a filter material was located in order to hold the clay layer and prevent the transition of fine clay particles. Over the filter material, the clay sample was kept under pressure in order to fix the 'absolute' permeability at 10^{-4}-10^{-6} cm/sec.

Under dynamic conditions, it is aimed to increase the possibility of the contact of clay particles with NaCN solution. These tests were carried out in a 400 ml beaker and 50 g clay sample was used in each experiment. During the experiments, the pH of the solution was controlled every hour and kept above 11,5. Cyanide ion concentration of the solutions was determined by $AgCl_2$ titration method and the absorption values are given as mg cyanide absorbed per 1 gram of clay.

EXPERIMENTAL

Static Column Tests

During static column tests, cyanide solution with a concentration of 1 g/L was placed over the clay layer with a particle size of -0.150 mm. The results were evaluated according to the ratio of initial concentration of the solution (g/L) to the final concentration (g/L). The results are given in Table IV.

Table IV. The static column tests results of the Bergama and the Kireçliköy samples

Time (Days)	Bergama $\sum$ Absorption - (%)	Kireçliköy $\sum$ Absorption - (%)
7	29.4	0
14	35.2	0
21	35.2	0
35	36.1	3.3
56	36.6	4.1

It is understood from the test results that the maximum cyanide absorption value of the Bergama clay was 36.6% and for the Kireçliköy sample no valuable absorption was observed though the experiment on this sample lasted 8 weeks.

Another measurable parameter for static column tests was the permeability coefficient, which is calculated by using CN^- ion concentrations of raffinate solution taken from the bottom of column in certain time intervals. The results of permeability calculations are shown in Table V.

Table V. Permeability coefficients for the Bergama and the Kireçliköy samples

Time (hour)	Bergama Permeability Coefficient (cm/s)	Kireçliköy Permeability Coefficient (cm/s)
24	5.67×10^{-6}	11.6×10^{-6}
48	5.61×10^{-6}	17.4×10^{-6}
72	5.36×10^{-6}	15.4×10^{-6}
96	5.12×10^{-6}	20.2×10^{-6}
120	4.72×10^{-6}	18.5×10^{-6}
144	4.67×10^{-6}	19.3×10^{-6}

The difference between the permeability properties of the Bergama and the Kireçliköy samples can be clearly seen from table 5 indicating that the permeability coefficient of the Bergama sample decreases with increasing time. Swelling of montmorillonite group clay particles via absorption of solution is thought to be the reason of this situation, however, the Kireçliköy sample has shown an opposite behavior with increasing permeability coefficient.

Dynamic Mixing Beaker Tests

In dynamic tests, the effect of pulp density, mixing time and particle size on absorption mechanisms of clay samples were investigated at four different cyanide concentrations (0.5, 1, 1.5, 2 g/L).

Mixing Time and Cyanide Concentration

During the tests where the effect of mixing time was investigated, pulp density was taken as 20 % and 2, 6 and 24 hour agitation times were tested. The maximum particle size of the test samples was -1 mm. The effect of cyanide concentration and agitation time on absorption behavior of clay samples can be seen in Figures 2, 3, 4 and 5.

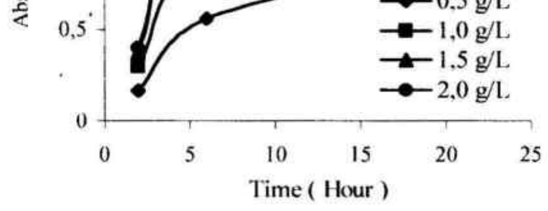

Figure 2. Agitation time versus specific absorption graph of the Bergama sample at different CN^- concentrations.

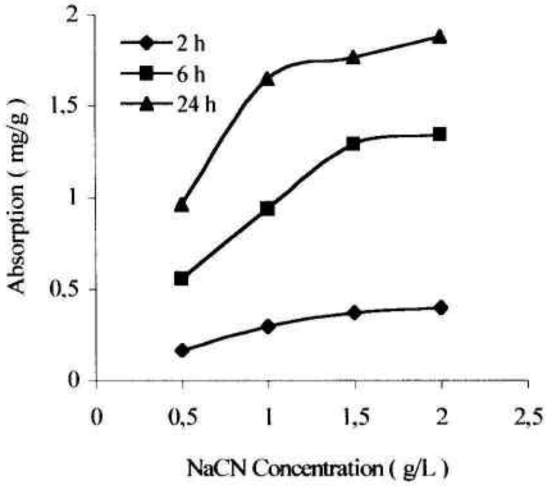

Figure 3. Cyanide concentration versus specific absorption graph of the Bergama sample.

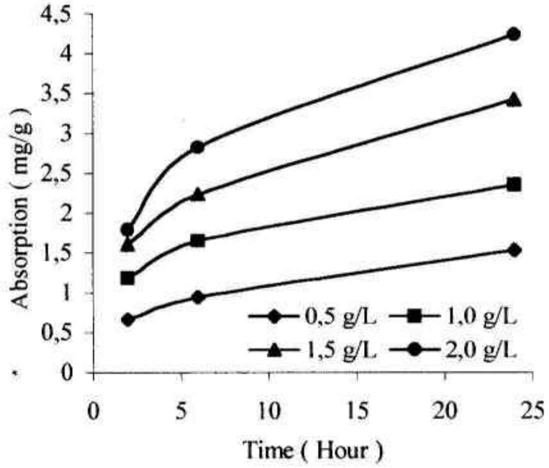

Figure 4. Agitation time versus specific absorption graph of the Kireçliköy sample.

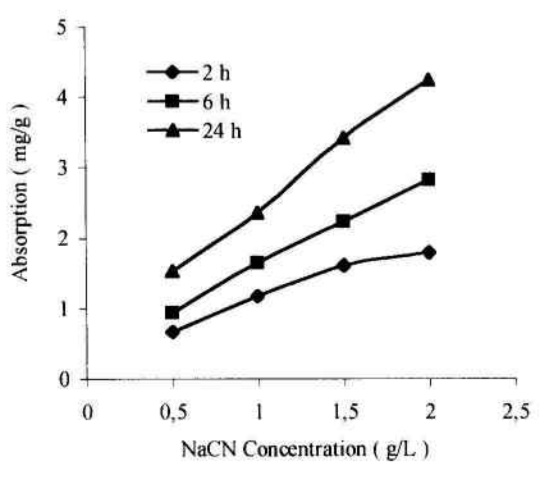

Figure 5. Cyanide concentration versus specific absorption graph of the Kireçlikoy sample.

It can be observed from the figures that specific absorptions of both clay samples were enhanced with increasing agitation time and cyanide concentration. Six hours was found to be the critical agitation time since the absorption rates of clay samples slow down over this value. Also the effect of agitation time on the change of critical cyanide concentration where the specific absorption rate of the Bergama sample starts to decrease can be deduced from figure 3. The Kireçliköy sample had a better absorption behavior with a maximum specific absorption value of 4.232 mg/g at the end of 24 hours agitation.

Effect of cyanide concentration was also tested at lower cyanide concentrations in order to determine the improvement of absorption capacities of clay samples by increasing cyanide concentration. The tests used 6 hours agitation time, 30% pulp density and -1 mm particle size and the results are presented in Figure 6.

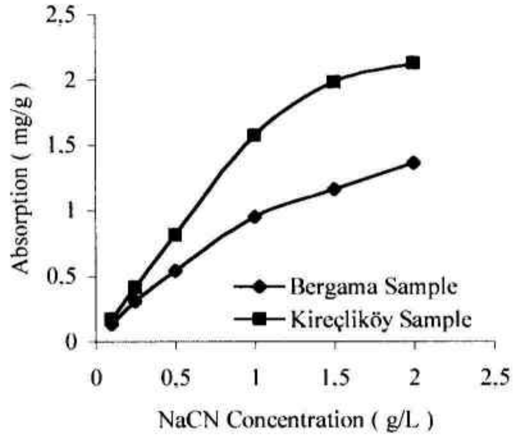

Figure 6. Effect of cyanide concentration on specific absorption.

Slopes of specific absorption vs. NaCN concentration curves start to decrease after 1 g/L NaCN concentration and then appear to reach saturation beyond 2g/L NaCN concentration indicating that absorption kinetics were getting slower above 1g/L.

Pulp Density

Pulp density is one of the primary important parameters since it influences the number of contacts between CN^- anions and clay particles. Agitation time and particle size were kept constant at 6 hours and -1 mm during the tests where the effect of pulp density was investigated. The results of the tests are given in and Figures 7 and 8.

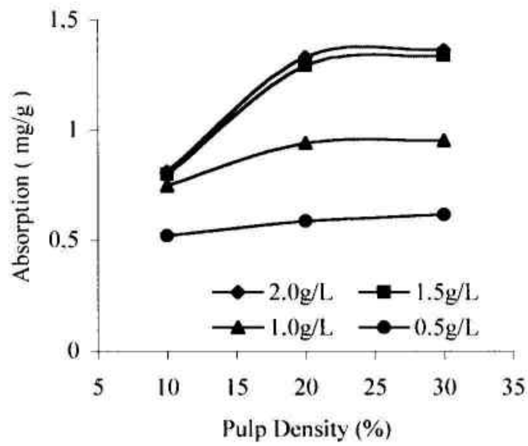

Figure 7. Effect of pulp density on specific absorption behavior of the Bergama sample.

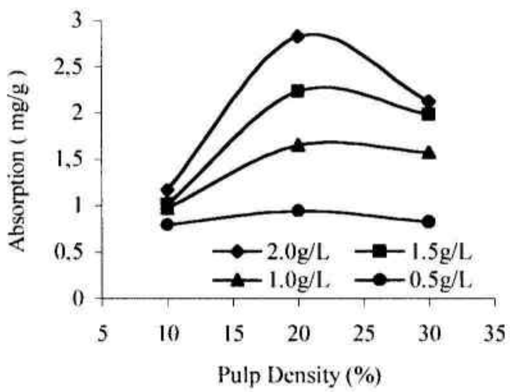

Figure 8. Effect of pulp density on specific absorption behavior of the Kireçlikoy sample

Tests with the Bergama sample indicate that 20% pulp density is a critical value and above this density, specific absorption could not be improved for all cyanide concentrations. But for the Kireçliköy sample 20% pulp ratio was found to be the peak point and over this value specific absorption of the sample decreases. This situation can be explained by the lack of diffusion due to the increasing viscosity of the pulp.

Particle Size

Absorption tests were conducted at three different size fractions in order to determine the effect of surface area as a function of particle size. During these tests 6 hours agitation time and 30% pulp density were chosen as the constant conditions and the Bergama sample was used as the test sample. The results of the tests are presented in Figure 9.

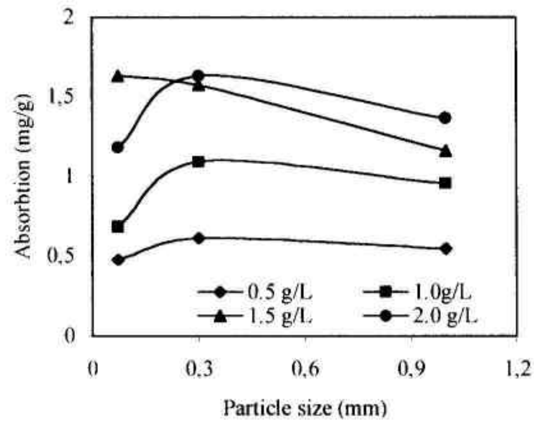

Figure 9. Particle size - specific absorption relationship for the Bergama sample.

As it can be seen from Figure 9, -0.3mm size fraction presented the maximum specific absorption values. This complex behavior of clay particles can be explained by the dispersion of particles into the original clay size (2 μm). Particle size analyses of -1 mm sized test sample showed that 41.7% of the sample was below 0.074 mm after 6 hours agitation while the -0.074 mm fraction of original sample was 11.6%. Test results indicate that cyanide absorption properties of the Bergama clay were negatively effected by relatively fine and coarse particle sizes.

CONCLUSIONS

Zeta potential measurements of the clay samples have presented negative values at given pH ranges disabling the electrostatic interactions between negative clay surface and cyanide anion. Under these circumstances, no surface adsorption mechanisms were expected.

Static column test results showed that the Bergama clay sample has performed better than the Kireçliköy sample in terms of absorption and permeability because of higher swelling behavior of montmorillonite.

The Kireçliköy clay sample has better absorption properties than the Bergama sample at dynamic regime. This was an expected conclusion when the higher porosity values of the Kireçliköy sample were taken into consideration.

As a result of the dynamic tests where the effects of agitation time and cyanide concentration were investigated, the critical agitation time was found to be about 6 hours for both clay samples. A critical cyanide concentration was also observed, where the specific absorption of the Bergama sample has reached at the saturation level. This saturation level was found to be different for various agitation times.

The effect of cyanide concentration was also tested at lower cyanide concentrations and at a different pulp density (30%). It can be concluded from the results that the change in pulp density has changed the level of saturation concentration.

Pulp densities of 10, 20, and 30% were tested during the experimental studies and it has been deduced that maximum specific absorption rates were obtained at 20% pulp density. The viscosity of the pulp increases to a higher level over 20% with the combined effect of swelling. Therefore, the contacts of cyanide ion and clay particles were disabled.

The effect of particle size on specific absorption was tested on the Bergama sample. It was found that the important parameter was not only the original particle size distribution of the clay sample but also the change of size distribution during the agitation period.

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