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# COMPARISON STUDIES BETWEEN CEMENT AND CEMENT-KAOLINITE PROPERTIES FOR INCORPORATION OF LOW-LEVEL RADIOACTIVE WASTES

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**ABSTRACT**

Comparison between the properties of cement and cement mixed with 7.5% kaolinite was performed to choose the most suitable matrix to incorporate radioactive wastes. The cement-kaolinite mixtures were prepared as uncured, cured, and heated specimens. The physical properties of the cement-kaolinite mixture, namely density, porosity, and water absorption percent, were determined. Compressive strength, infrared spectra, thermal analysis, and the effect of gamma rays on the samples were studied. The studies were extended to the cement-kaolinite mixture in the presence of some chemical additives at different concentrations. Leachability of radioactive isotopes from the cement-kaolinite mixture was measured as a function of time. The physical and mechanical properties of cement were decreased in the presence of 7.5% kaolinite, whereas $^{137}Cs$ and $^{60}Co$ were less leached from the cement-kaolinite mixture. © *1997 Elsevier Science Ltd*

## Introduction

Cement is used in the immobilization processes to incorporate radioactive isotopes from radioactive wastes due to its low coasts noncombustibility, self-shielding, and its high mechanical properties (1,2). Moreover, radioactive wastes are either sludges or resins mixing with chemicals that could affect the strength properties of cement and thus increase the release of incorporated isotopes from cement (3–5). Conversely, the published data (6,7) showed that silicate clays can fix radioactive elements due to their adsorption properties and accordingly decrease the leaching rates when mixed with cement.

The present work investigates the effect of some chemicals on the physical, mechanical, and thermal properties of the cement-kaolinite mixture.

## Experimental

The cement used was ordinary Portland cement. The percentage chemical analysis of cement as certified by National Portland Cement Company, Helwan, Cairo, Egypt, was as follows:

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CaO, 61.01; $SiO_2$, 19.84; $Al_2O_3$, 4.47; $Fe_2O_3$, 4.0; MgO, 2.5; $K_2O$, 0.60; and $SO_2$, 2.48 (8). The kaolinite was obtained from Aswan region, Egypt. The percentage chemical analysis of the kaolinite as certified by Arab-Swiss Engineering Company was as follows (9): $SiO_2$, 71.69; $Al_2O_3$, 16.24; $Fe_2O_3$, 1.43; CaO, 0.16; MgO, 0.23; $SO_3^-$, 0.85; $K_2O$, 0.44; $Na_2O$, 0.01; $Cl^-$, 0.01; and $TiO_2$, 1.79.

Hydrochloric acid, sulphuric acid, nitric acid, sodium hydroxide, citric acid, boric acid, oxalic acid, acetic acid, trisodium phosphate, tributylphosphate, ethylenedi-aminetetra-acetic acid, and sodium sulphate were prepared as stock solutions using analytical grade reagent. Simulated radioactive borate waste solution was prepared by mixing the following amount (in g/L): $Na^+$, 23.9; $K^+$, 7.2; $Cl^-$, 1.6; $CO_3^-$, 12.3; $NO_3^-$, 34.5; $BO_2^-$, 26.1; boric acid, 92.4; oxalate and citrate, 0.15; and 10 Bq of $^{137}Cs$ and $^{60}Co$.

Cement and kaolinite were sieved then mixed together in dry form, at known ratios, and either water or chemical solutions were added at ratio W/C = 30% until homogenous phase was obtained. Prespex cubic molds of dimensions 7 × 7 × 7 cm was used to prepare the tested cement and cement-kaolinite specimens.

Physical properties of specimens such as density, porosity percent, absorption percent, setting times (initial and final), and heat of hydration were investigated using a densitometer and a vicat apparatus. Infrared studies were carried out in the range from 600 $cm^{-1}$ to 4000 $cm^{-1}$. The differential thermal analysis and thermogravimetric analysis (DTA and TGA) were performed at room temperature (25 ± 3°C) until 500°C with heating rate of 20°C/min.

Samples of cement and cement-kaolinite were irradiated using gamma rays emitted from a $^{60}Co$ cell of activity 0.5 M rad/h at different doses.

Static leaching was carried out according to Hespe's method (10) using distilled water as a leaching solution. The samples were prepared as cubes with dimensions 2 × 2 × 2 cm. Leaching experiments of $^{60}Co$ or $^{137}Cs$ from cement or cement-kaolinite samples were carried out. The released isotopes produced from the leaching effect were investigated using a multichannel gamma analyzer spectrometer of 4″ × 4″ NaI (Tl) crystal.

## Results

The density of both hydrated cement and cement mixed with kaolinite was found to be about 2.1 ± 0.2 $g/cm^3$. A noticed decrease in the density of cement mixed with kaolinite was observed when organic chemicals were added (Table 1). The absorption and porosity percents of cement mixed with kaolinite increased as the chemicals concentration increased. Initial and final setting times for cement in the presence of 7.5% kaolinite mixed with 30% water occurred after 140 min and 210 min, respectively. The addition of inorganic chemicals to the specimen decreased the setting times, while organic compounds such as; citric acid, oxalic acid, and EDTA (ethelynediaminetetra-acetic acid) increased the setting times. Moreover as the chemical concentration increased, the setting times decreased.

Compressive strength values for cured, uncured and heated cement, cement-kaolinite, and cement-kaolinite mixed with chemicals were given in Table 2. The presence of kaolinite or chemicals in cement decreased the compressive strength values. As the chemical concentration increased the compressive strength decreased. The decrease in the compressive strength is a result of the interaction between added chemicals and calcium ions of hydrated cement (gel or $Ca(OH)_2$). Cured samples had higher compressive strength values than uncured and heated

TABLE 1
Physical properties of hydrated cement, cement-kaolinite mixture, and cement-kaolinite mixed with different chemicals

| Chemicals added to cement + water + kaolinite | Conc. % | Density g/cm$^3$ | Porosity % | Absorption | Setting Times (min) Initial | Final |
|---|---|---|---|---|---|---|
| Cement | 0.0 | 2.1 | 16.98 | 11.35 | 60 | 240 |
| Cement + kaolinite | 0.0 | 2.05 | 19.94 | 16.70 | 50 | 225 |
| HCl | 5 | 2.01 | 26.00 | 15.60 | 65 | 265 |
| | 10 | 2.00 | 28.20 | 16.80 | 75 | 285 |
| | 15 | 1.92 | 30.80 | 18.80 | 80 | 290 |
| $H_2SO_4$ | 1 | 1.95 | 36.10 | 26.20 | 45 | 180 |
| | 2 | 1.90 | 38.70 | 28.60 | 40 | 160 |
| | 3 | 1.82 | 42.20 | 32.20 | 35 | 105 |
| $HNO_4$ | 1 | 1.95 | 42.60 | 20.60 | 50 | 220 |
| | 3 | 1.90 | 46.40 | 24.40 | 40 | 190 |
| | 5 | 1.84 | 48.80 | 26.50 | 35 | 165 |
| NaOH | 1 | 1.91 | 25.20 | 15.10 | 50 | 190 |
| | 3 | 1.85 | 27.30 | 16.90 | 45 | 165 |
| | 5 | 1.80 | 30.20 | 19.50 | 40 | 140 |
| $Na_2SO_4$ | 1 | 1.97 | 25.80 | 13.20 | 55 | 215 |
| | 3 | 1.97 | 27.20 | 15.20 | 50 | 190 |
| | 5 | 1.87 | 29.20 | 16.80 | 40 | 175 |
| $Na_3PO_4$ | 1 | 2.00 | 24.40 | 17.30 | 65 | 190 |
| | 3 | 1.97 | 26.20 | 18.90 | 75 | 230 |
| | 5 | 1.91 | 29.10 | 20.40 | 80 | 285 |
| TBP | 1 | 2.01 | 30.20 | 16.80 | 75 | 220 |
| | 3 | 1.98 | 32.30 | 17.20 | 90 | 235 |
| | 5 | 1.91 | 35.20 | 18.20 | 110 | 250 |
| Citric acid | 0.5 | 2.00 | 42.00 | 23.00 | 90 | 240 |
| | 1 | 1.91 | 44.00 | 26.00 | 150 | 630 |
| | 3 | 1.85 | 00.00 | 00.00 | 480 | 1080 |
| Boric acid | 1 | 1.92 | 34.80 | 20.80 | 190 | 260 |
| | 3 | 1.86 | 38.20 | 24.20 | 120 | 330 |
| | 5 | 1.74 | 40.20 | 28.20 | 135 | 275 |
| Oxalic acid | 1 | 2.00 | 31.30 | 21.20 | 75 | 290 |
| | 3 | 1.93 | 36.80 | 24.80 | 90 | 330 |
| | 5 | 1.81 | 39.70 | 26.90 | 120 | 375 |
| Acetic acid | 1 | 1.93 | 35.00 | 24.40 | 50 | 185 |
| | 3 | 1.81 | 42.20 | 30.70 | 45 | 170 |
| | 5 | 1.68 | 45.20 | 34.20 | 40 | 155 |
| EDTA | 1 | 2.00 | 34.60 | 20.10 | 95 | 320 |
| | 3 | 1.85 | 37.20 | 23.10 | 150 | 325 |
| | 5 | 1.74 | 39.70 | 28.20 | 200 | 390 |

specimens, respectively. The addition of organic chemical compounds to cement samples destroyed cement bonds. The added organic compounds have the ability to form chelates or complexes with calcium ions of cement, thus destroying its physical and mechanical properties.

TABLE 2
The compressive strength of hydrated cement, cement-kaolinite mixture and cement-kaolinite mixed with different chemicals

| Chemical added to cement + water + kaolinite | Conc. % | Maximum Compressive Strength $Kg/Cm^2$ Uncured | | | | Cured | | | | Heated | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 3d | 7d | 14d | 28d | 3d | 7d | 14d | 28d | 3d | 7d | 14d | 28d |
| Cement + water | 0.0 | 470 | 555 | 650 | 700 | 495 | 590 | 730 | 780 | 520 | 590 | 640 | 660 |
| Cement + kaolinite | 0.0 | 410 | 470 | 530 | 555 | 420 | 510 | 680 | 730 | 450 | 520 | 650 | 580 |
| HCl | 5 | 320 | 370 | 420 | 450 | 380 | 455 | 580 | 670 | 370 | 375 | 410 | 440 |
| | 10 | 290 | 310 | 390 | 400 | 340 | 430 | 535 | 630 | 345 | 350 | 395 | 400 |
| | 15 | 260 | 280 | 325 | 375 | 300 | 400 | 510 | 590 | 320 | 340 | 370 | 355 |
| $H_2SO_4$ | 1 | 260 | 350 | 400 | 390 | 270 | 360 | 450 | 450 | 300 | 350 | 360 | 365 |
| | 2 | 190 | 240 | 270 | 245 | 185 | 250 | 280 | 260 | 200 | 265 | 285 | 290 |
| | 3 | 125 | 180 | 210 | 190 | 110 | 160 | 200 | 195 | 105 | 165 | 210 | 210 |
| $HNO_3$ | 1 | 380 | 430 | 500 | 510 | 400 | 450 | 535 | 630 | 400 | 450 | 485 | 285 |
| | 3 | 360 | 385 | 460 | 480 | 360 | 420 | 505 | 610 | 365 | 400 | 400 | 427 |
| | 5 | 315 | 340 | 430 | 455 | 330 | 400 | 480 | 555 | 300 | 350 | 360 | 360 |
| NaOH | 1 | 295 | 350 | 390 | 390 | 310 | 350 | 385 | 395 | 290 | 345 | 340 | 250 |
| | 3 | 235 | 280 | 350 | 360 | 290 | 290 | 290 | 300 | 170 | 250 | 280 | 280 |
| | 5 | 88 | 150 | 165 | 180 | 100 | 135 | 300 | 225 | 125 | 150 | 180 | 180 |
| $Na_2SO_4$ | 1 | 400 | 425 | 470 | 480 | 395 | 440 | 485 | 515 | 390 | 420 | 430 | 450 |
| | 3 | 320 | 400 | 420 | 460 | 350 | 410 | 440 | 480 | 335 | 380 | 400 | 420 |
| | 5 | 230 | 240 | 295 | 315 | 245 | 280 | 330 | 385 | 225 | 235 | 260 | 290 |
| $Na_3PO_4$ | 1 | 340 | 420 | 450 | 500 | 390 | 440 | 480 | 560 | 320 | 350 | 360 | 400 |
| | 3 | 250 | 320 | 390 | 420 | 280 | 390 | 430 | 440 | 390 | 310 | 340 | 370 |
| | 5 | 180 | 240 | 310 | 340 | 220 | 300 | 360 | 380 | 265 | 290 | 290 | 300 |
| Citric acid | 1 | 365 | 425 | 530 | 490 | 360 | 430 | 85 | 520 | 352 | 395 | 410 | 415 |
| | 3 | 265 | 335 | 490 | 368 | 260 | 370 | 406 | 425 | 285 | 295 | 310 | 310 |
| | 5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Boric acid | 0.5 | 345 | 390 | 430 | 450 | 65 | 480 | 580 | 650 | 310 | 390 | 415 | 450 |
| | 1 | 295 | 310 | 350 | 380 | 340 | 450 | 550 | 600 | 260 | 285 | 295 | 300 |
| | 3 | 115 | 135 | 200 | 250 | 250 | 360 | 540 | 550 | 87 | 88 | 85 | 120 |
| Oxalic acid | 1 | 300 | 340 | 425 | 450 | 325 | 415 | 480 | 520 | 360 | 20 | 425 | 430 |
| | 3 | 260 | 300 | 350 | 380 | 270 | 360 | 400 | 440 | 270 | 300 | 335 | 340 |
| | 5 | 220 | 260 | 300 | 340 | 185 | 270 | 335 | 340 | 200 | 230 | 250 | 260 |
| Acetic acid | 1 | 360 | 420 | 450 | 480 | 320 | 465 | 570 | 600 | 305 | 380 | 420 | 430 |
| | 3 | 280 | 305 | 400 | 420 | 270 | 400 | 475 | 490 | 270 | 310 | 375 | 390 |
| | 5 | 240 | 290 | 350 | 360 | 190 | 170 | 335 | 350 | 225 | 260 | 290 | 310 |
| EDTA | 1 | 290 | 320 | 330 | 360 | 295 | 330 | 390 | 400 | 280 | 305 | 310 | 330 |
| | 3 | 250 | 265 | 285 | 300 | 240 | 300 | 350 | 360 | 205 | 240 | 260 | 275 |
| | 5 | 200 | 235 | 230 | 230 | 190 | 235 | 250 | 260 | 175 | 200 | 210 | 225 |
| TBP | 1 | 310 | 360 | 370 | 380 | 290 | 360 | 390 | 420 | 250 | 280 | 325 | 340 |
| | 3 | 280 | 325 | 330 | 350 | 270 | 330 | 350 | 370 | 220 | 250 | 280 | 300 |
| | 5 | 215 | 235 | 260 | 280 | 235 | 275 | 335 | 350 | 170 | 210 | 250 | 260 |
| Simulated waste | 0.75 | 160 | 320 | 365 | 390 | 190 | 345 | 385 | 460 | 135 | 265 | 275 | 290 |
| | 1.5 | 150 | 215 | 230 | 245 | 170 | 270 | 295 | 420 | 100 | 140 | 150 | 170 |
| | 3.0 | 130 | 185 | 195 | 200 | 150 | 215 | 230 | 300 | 60 | 65 | 75 | 100 |
| | 6.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

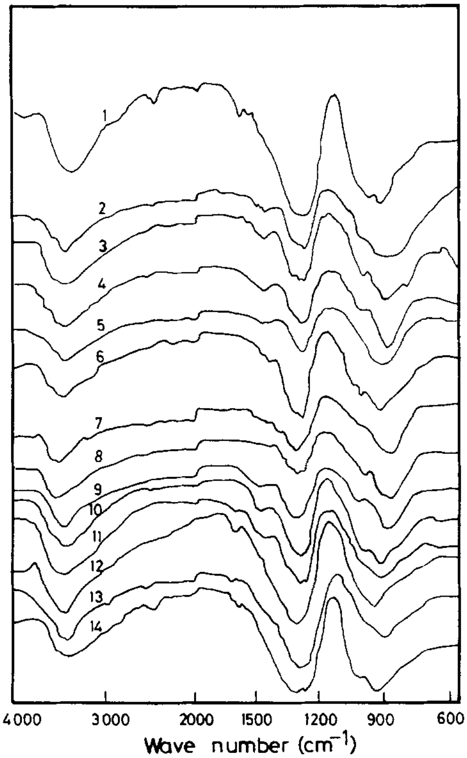


FIG. 1.
IR spectra of (*1*) hydrated cement, (*2*) cement-kaolinite, and cement kaolinite mixed with (*3*) 15% HCl, (*4*) 3% $H_2SO_4$, (*5*) 5% $HNO_3$, (*6*) 5% NaOH, (*7*) 5% $Na_2SO_4$, (*8*) 5% acetic acid, (*9*) 3% citric acid, (*10*) 5% oxalic acid, (*11*) 5% boric acid, (*12*) 5% TBP, (*13*) 5% EDTA, and (*14*) 50% simulated borate waste.

The infrared spectra of cement (Fig. 1) showed the presence of absorbed peaks near 3400 cm$^{-1}$, 1660 cm$^{-1}$, 1440 cm$^{-1}$, and 1100 cm$^{-1}$, which are mainly due to the vibration of the hydrogen bond of free water molecules in cement. The infrared spectra has also peaks at 925 cm$^{-1}$, 835 cm$^{-1}$, 520 cm$^{-1}$, and 465 cm$^{-1}$ due to vibration of water in the $C_2S$, $C_3S$, and Al-O of cement. The band at 1100 cm$^{-1}$ is due to sulphate. The infrared spectra of cement mixed with chemicals are all similar to cement spectra (11). Therefore it can be stated that the chemical added to cement kaolinite mixtures could combine to both water attached to hydrated cement (C-S-H) ($C_2S$, $C_3S$, and Al-O) and water in carbonates and calcites of hydrated cement samples.

The thermogravimetric analysis (TGA) results (Table 3) showed that the weight loss in hydrated cement-kaolinite was about 5% at 500°C. Chemicals added to cement increased the weight loss of samples to 8% at 500°C. The differential thermal analysis diagrams (DTA) of hydrated cement-kaolinite samples (Figs. 2a and b) showed an endothermic peak at 80–100°C, which is related to free water in the specimen (12). The DTA of cement-kaolinite or cement-kaolinite mixed with chemicals showed an exothermic peak at 280°C-350°C due to the presence of water molecules that are strongly bounded to calcium hydroxide in hydrated cement (13).

Figure 3 shows the compressive strength for some of the studied samples after gamma

TABLE 3
The weight loss of hydrated cement, cement-kaolinite and cement-kaolinite mixed with different chemicals

| Samples | Weight loss % |
|---|---|
| Cement | 4.97 |
| Cement + kaolinite | 4.92 |
| 15% HCl | 8.02 |
| 3% $H_2SO_4$ | 5.60 |
| 5% $HNO_3$ | 7.14 |
| 5% NaOH | 5.22 |
| 5% $Na_2SO_4$ | 6.37 |
| 5% $Na_3PO_4$ | 7.54 |
| 5% TBP | 5.99 |
| 3% Citric acid | 4.56 |
| 5% Boric acid | 5.15 |
| 5% Oxalic acid | 5.42 |
| 5% Acetic acid | 7.17 |
| 5% EDTA | 7.60 |

irradiations to certain absorbed doses. As the absorbed gamma dose increased, the compressive strength and the density of samples decreased. Such effect was clearly remarked in the case of adding chemicals to cement that decrease the cement properties.

Leachability studies showed that the presence of kaolinite in cement decreased the amount of radioisotope released (Fig. 4). As the amount of nonactive salt increased in the cement-kaolinite mixture, the leachant amount percent increased. This is due to the competition between the active and nonactive ions to release from cement. The presence of chemicals in the cement-kaolinite mixture increased also the leachant percent. Previous studies (6,7) showed that kaolinite could adsorb radioactive isotopes on the gel or $Ca(OH)_2$ of hydrated cement, thus decreasing the release of such ions from the cement-kaolinite mixture.

## Conclusion

From the obtained results, it can be seen that ordinary cement has a higher compressive strength value than cement in the presence of 7.5% kaolinite. Chemicals added to cement-kaolinite decreased the strength and physical properties of cement-kaolinite. As the concentration of chemicals increased, the compressive strength of cement samples decreased while leachability of radioisotopes from cement-kaolinite decreased.

The cement-kaolinite mixture is a suitable matrix material to immobilize low-level radioactive wastes. The chelating agents or organic compounds should be avoided to mix with the cement mixture, because there is a complete deficiency of the properties of cement. Moreover, the 1% of inorganic compounds could be incorporated in the cement-kaolinite paste. The presence of 7.5% of kaolinite to cement improved the conditioning properties of cement. Therefore, it can be recommended that the addition of kaolinite to cement at a ratio of 7.5%

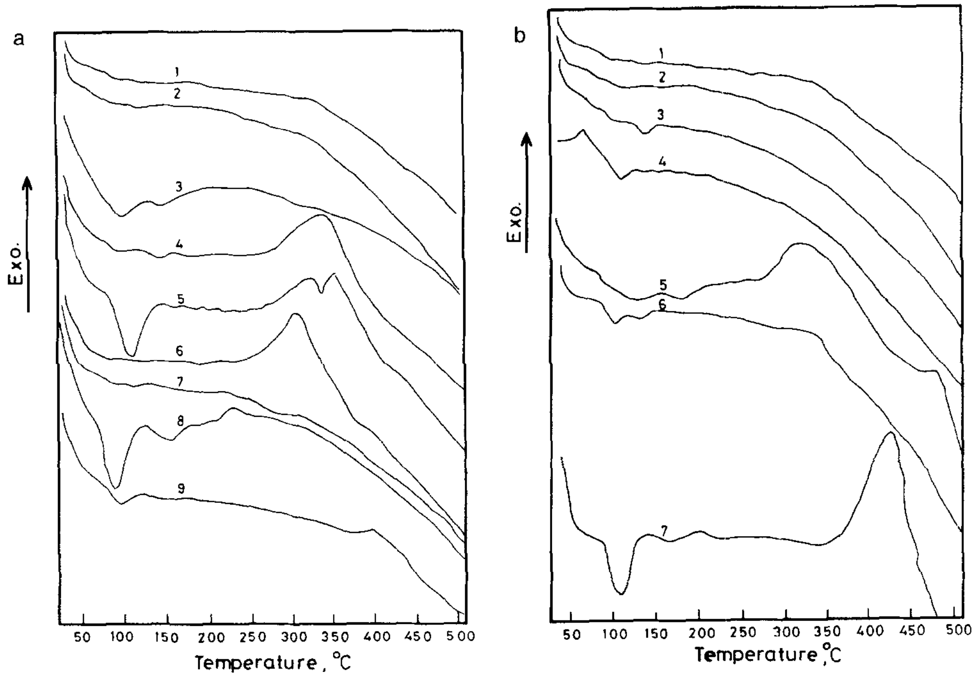


FIG. 2.

(*a*) DTA thermographs of (*1*) hydrated cement, (*2*) cement-kaolinite, and cement kaolinite mixed with (*3*) 15% HCl, (*4*) 3% $H_2SO_4$, (*5*) 5% $HNO_3$, (*6*) 5% NaOH, (*7*) 5% $Na_2SO_4$, (*8*) 5% $Na_3PO_4$, and (*9*) 3% citric acid. (*b*) DTA thermographs of (*1*) hydrated cement, (*2*) cement-kaolinite, and cement-kaolinite mixed with (*3*) 5% boric acid, (*4*) 5% EDTA, (*5*) 5% oxalic acid, (*6*) 5% TBP, and (*7*) 5% acetic acid.

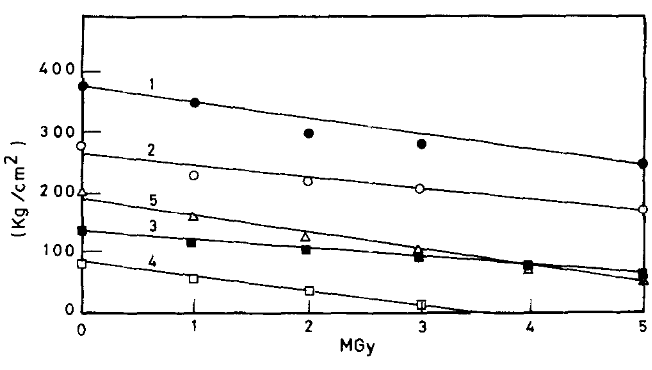


FIG. 3.

The effect of gamma absorbed doses on the compressive strength of (*1*) cement-kaolinite and cement-kaolinite mixed with (*2*) 15% HCl, (*3*) 5% NaOH, (*4*) 1% citric acid, and (*5*) 0.75% simulated borate waste.

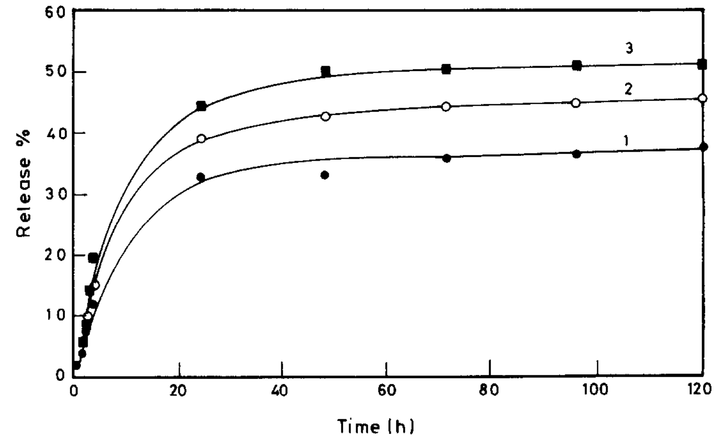


FIG. 4.

Leaching of $^{137}Cs$ from the cement-kaolinite mixture in the presence of different percents of CsCl (0.2, 0.4, and 0.6).

improves the leaching properties of cement when low-level radioactive waste sludges were immobilized.

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