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# Physicochemical Evaluation of Soil-Cement by X-Ray Fluorescence: Percentage-Based Data

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**Abstract:** Cement Deep mixing method applied in Lowland areas, is often set at W/C = 1.0. Also, W/C is determined based on empirical experience so far, and Engineers seem reluctant to increase the amount of water (w/c > 1). They have concerns over the possibility of insufficient mechanical strength of improved soil columns due to the amount of water. So, based on X-ray fluorescence data analysis instrument, our research is dealing with the evaluation of the chemical composition of elements responsible for soil-cement hardening on six specimens with parameters such as W/C ratio, the amount of cement C, the curing, and the mixing times. Then, the main components identified and quantified that interest us are silicon dioxide, calcium oxide, alumina, iron oxide and magnesium oxide. Especially about the amount of silica and calcium oxide which most influence the hardening process of the soil cement, we have the uniform tendencies of its percentage for W/C = 1.5 after 10min of mixing time and when the curing time becomes important (28 days). Then, combined with the strength $q_u$ distribution at 100 different points of each specimen, taken by needle penetration, the one with W/C = 1.5 and C = 110 kg/m$^3$ is more uniform than the others. Finally, W/C = 1.0 is not the most effective ground improvement specification to consider when performing deep mixing treatment on cohesive soft soil such as Ariake clay.

**Key words:** physico-chemical evaluation, soil-cement, Ariake clay, X-ray fluorescence, W/C

## 1. Introduction

Soil improvement by shallow and deep mixing method (DMM) involved the mechanical mixing of cement or lime with the clayey or silty soils. Soil-Deep-Mixing is a method which consists in using the soil already in place on a construction site to carry out geotechnical works by means of a mechanical mixture with a binder, here the cement [1].

Physico-chemical properties of the soil can be affected by the type of raw materials that form this soil or by various human activities or industrial waste deposits. Cement mixed with the soil will therefore significantly affect the physico-chemical properties of that soil. The production of cement which includes the extraction of raw materials, which are mainly oxides and carbonates of metals, involves grinding the raw materials into fine particles, such as limestone, shale, sand, clay, ore iron and fly ash, then mixing them in proper proportions [2].

Cement Deep mixing method applied in Lowland areas in Japan, is empirically set at W/C = 1.0 and according to [3], with an amount of cement C and a design standard strength $\overline{q_u}$ range respectively between 50-150 kg/m$^3$ and 500-1000 kN/m$^2$. However, engineers seem reluctant to increase the amount of water (W/C > 1) used, because they have concerns over the possibility of vertical and horizontal displacement of improved soil columns due to the amount of water. This study is not only to deeply

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understand the link between the mixing time, the curing time, with the chemical compounds responsible for hardening, but especially to know the conditions for a better distribution of the strength inside the soil, in the case of Ariake clay. A soft cohesive geomaterial with high natural water content only finest particles used in the Kyushu region. We will focus on the evaluation of the physico-chemical compounds of soil-cement by using x-ray fluorescence (XRF) data analysis. With XRF technology, it is possible to quickly conduct a multi-element analysis of a sample by exposing a sample of the testing material to an x-ray source. The elements in a sample emit a specific x-ray signature, unique to that element, and by counting the number or intensity of the wavelength, and the intensity of this signature, it is possible to make quantitative measurements of elements in the sample [4].

Our approach is to evaluate the chemical components by considering the reactions which exist between these components in the solidification of the soil-cement materials and states that when performing deep mixing treatment on soft cohesive soil such as Ariake clay, if W/C = 1.0 is the most effective ground improvement specification.

## 2. Materials and Methods

### *2.1 Materials and Equipment*

The material and equipment of our study is the soil-cement which is composed of a mixture of Ariake clay and cement at different water-cement ratios, and the X-ray fluorescence instrument which has its roots in geology.

On the one hand, the clay soil of Saga prefecture called Ariake clay, which is a very soft sensitive clay, is in the coastal plain around Ariake bay, in the northwestern part of the island of Kyushu in Japan [5]. The mechanical properties of Ariake clay such as the unconfined compressive strength are between 3 kPa and 30 kPa for the upper layer of above 10 meters depth and between 30 kPa and 100 kPa for the lower layer, and the axial strain at failure, between 2% to 4% for the undisturbed soil [6]. When Ariake clay specimens are remolded, most of them become in a liquid state. It is used for the preparation of soil-cement specimens after the incorporation of cement and its mixing, these specimens are used for testing after a duration of curing for different mixing times.

On the other hand, the X-ray fluorescence data analysis instrument (Fig. 1) is used to analyze the chemical composition of the material laid on a flat rectangular bowl of 27 cm × 21 cm × 3.5 cm dimensions (Fig. 2). Divisions are made to facilitate measurements with the hand-held fluorescent x-ray.

**Fig. 1 X-ray fluorescence analysis instrument [13].**

**Fig. 2 Flat rectangular bowl to keep the solidifying material.**

### 2.2 Methods

For the x-ray fluorescence data analysis, we consider for the three samples X, Y and Z the two conditions for our parameter i = {1 min; 10 min}, the mixing time. Then for the six flat rectangular bowl of solidifying material, we do the measurement with the x-ray fluorescence equipment for each value of the parameter j, where j = {1 hour; 2hours; 7 days; 14 days; 28 days} is the curing time of the solidifying material. So, we stand by S the set of the considered samples. X, the sample with C = 110 kg/m$^3$ amount of cement and W/C = 1.0; Y, the sample with C = 110 kg/m$^3$ amount of cement and W/C = 1.5; and Z, the sample with C = 80 kg/m$^3$ amount of cement and W/C = 1.5. Let iSj be the set of samples in our study such as iSj = {iXj; iYj; iZj}. We have for instance $_1X_2$, the Ariake clay specimen from the sample where C = 110 kg/m$^3$ and W/C = 1.0, at 1min of mixing time and 2 hours of curing time. $_{10}Y_7$ is the one from the sample which has C = 110 kg/m$^3$ and W/C = 1.5, at 10 min of mixing time and 7 days of curing time. And finally, to stop with three examples, $_{10}Z_{28}$, the one where C = 80 kg/m$^3$ and W/C = 1.5, at 10min of mixing time and after 28 days of curing time.

Then, the preparation of the mixture to the curing of the specimens is done as follows.

Weigh the sample, and the cement-based solidifying material, a predetermined amount of mixed water.

Specify the W/C ratio and thoroughly mix the solidifying material and kneading water.

Mix the solidifying material and the kneading water sufficiently at the specified W/C ratio. In order to match the conditions before mixing, set the solidifying material slurry in the mixing container (Fig. 3) so that it is sandwiched between two layers of samples.

Mix to obtain a soil treated with a uniform cementitious solidifying material. The standard mixing time is about 10 min [3] .So, the mixing times are 1 min and 10 min for our case.

**Fig. 3 Soil-cement mixing equipment.**

Soil treated with a cement-based solidifying material is laid out in a flat rectangular bowl which contents some divisions to facilitate measurement,

Then, after the curing time, we use hand-held X-ray fluorescent (Fig. 1) and needle penetration (Fig. 4), types of equipment to make the measurements.

**Fig. 4 Needle penetration equipment.**

## 3. Results and Discussion

### *3.1 Results, and Interpretation*

The main elements identified and quantified in soil-cement in the case of this study are Al, Ca, Fe, K, Si, S, Ti, Mn, Zn and Sr (respectively Aluminum, Calcium, Iron, Potassium, Silicon, Sulfur, Titanium, Manganese, Zinc, and Strontium). However, the main components we assume to consider are Silicon dioxide ($SiO_2$), Calcium oxide (CaO), Alumina ($Al_2O_3$), Iron oxide ($Fe_2O_3$) and magnesium oxide (MgO). Because the X-ray fluorescence equipment does not consider oxygen when identifying and quantifying the chemical elements in the sample. So, considering the percentage-based data, for each sample X, Y and Z, the general observation that one can make from all the graphs is that the shapes are globally similar for 1 min or 10 min mixing time. And a particular point from the curves, especially for CaO, where the behavior of the curves is reversed, compared to the point about $SiO_2$. And the amount of CaO is higher with the mixing time and the curing time. It means that the longer is the mixing and curing time, higher is the amount of CaO for all samples. So, there is a transformation between the chemical elements especially with the calcium. $SiO_2$ and CaO are the main components in soil-cement which have the greatest influence on the hardening of this material.

Particularly about sample X, for only 1min of mixing time, one can notice two categories of tendencies, especially by $SiO_2$ content. So, the two curves (1 hour and 2 hours of curing time) are quite similar too, on the one hand. And the third others (7, 14, and 28 days of curing time) curves are close similar, on the other hand. But, for 10 min of mixing time, it is a little complicated to talk about two categories, all the curves follow the same flow in general, except the curve for 1 hour of curing which seems to be separated. That means, for 10 min of mixing time, the chemical components are better distributed inside the sample.

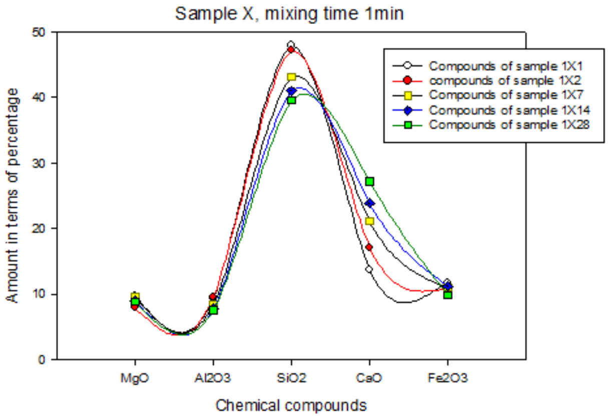

**Fig. 5 Sample X chemical components after 1 min of mixing.**

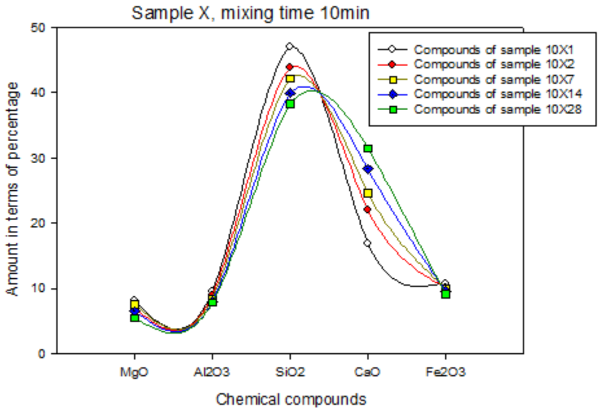

**Fig. 6 Sample X chemical components after 10 min of mixing.**

For sample Y (Fig. 7 and Fig. 8), we can divide the curves into two trends, one with (1 hour, 2 hours, 7 days, and 14 days of curing time) curves, and the other is the 28-days' curve. Because there is an important gap between them. However, for 10min of mixing time, the gap between the curves is reduced (very less) and all the curves follow the same trend. It means the chemical components are better distributed inside that sample. Even for 1 min of mixing time only one curve is not so close to the others. And for 10 min of mixing time, they are well distributed inside the sample. The fluidity of the binder used in this sample (W/C = 1.5), made it easier to mix and disperse the chemical agents into the soil sample.

What about sample Z (Fig. 9 and Fig. 10)? For 1min mixing time, except for two curves that follow the same trend (1 hour, 2 hours of curing time), the other ones are very disparate and go their own way.

While, for 10 min of mixing time, all the curves are in the same trend. It is because for 10 min mixing the chemical components are better distributed than for 1 min of mixing time. In addition, the small amount of cement did not allow the binder to spread well in the soil sample, despite its fluidity. But it became better with the duration of the mixing.

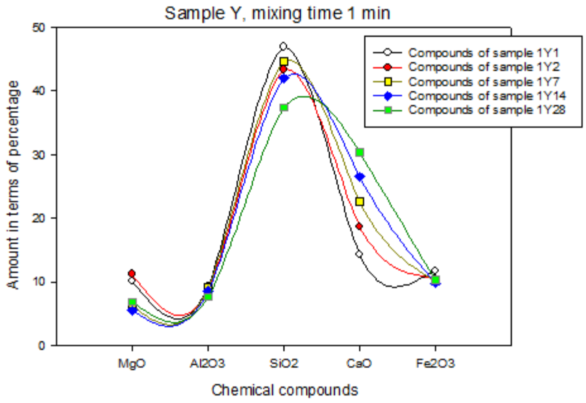

**Fig. 7 Sample Y chemical components after 1 min of mixing.**

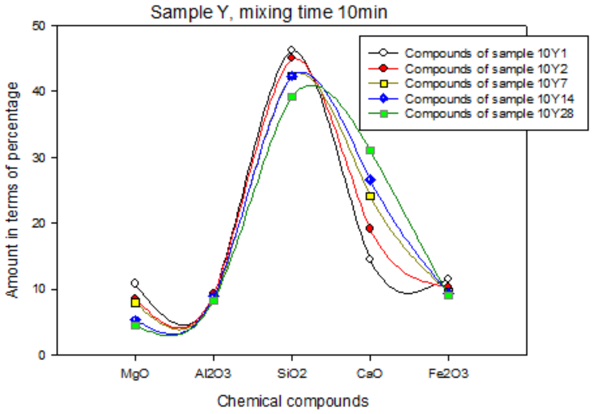

**Fig. 8 Sample Y chemical components after 10 min of mixing.**

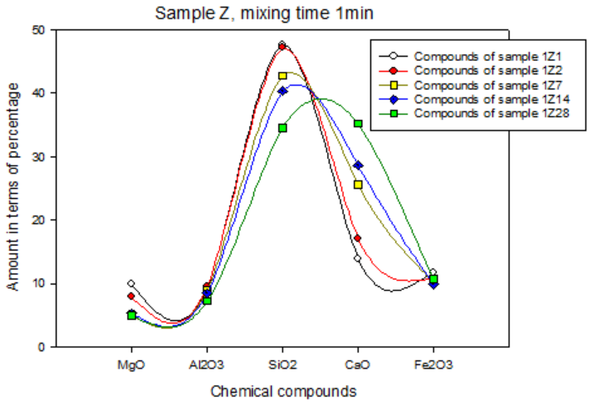

**Fig. 9 Sample Z chemical components after 1 min of mixing.**

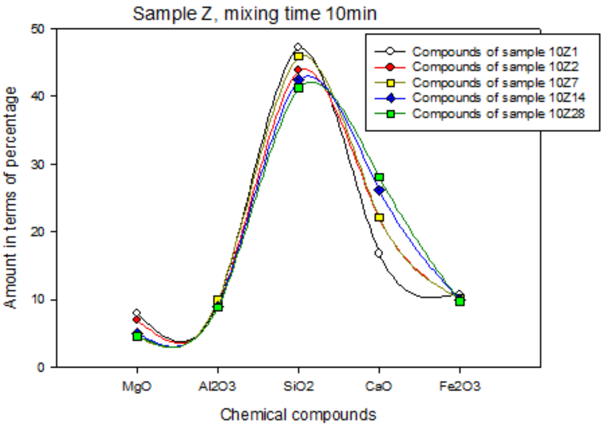

**Fig. 10 Sample Z chemical components after 10 min of mixing.**

Finally, when we consider the three samples (Fig. 11), after 10 min of mixing time and 28 days of curing time, we notice that there are two curves that are very close to the point of $SiO_2$ content (samples X and Y) and are almost overlapped. However, the other (sample Z) is detached from the other two.

In addition, after 28 days of curing time, we check by the needle penetration index (NPI), the corresponding strength in 100 points (Count) on each sample. We stand by $CoV$ the coefficient of variation in percentage, $q_{max}$ and $q_{min}$ are the corresponding strengths (respectively the maximum et minimum values). The table above shows the summary data of observed points. For 1 min of mixing time, sample Z has the greatest strength (1752 $kN/m^2$) with also the greatest $CoV$ (75.9%), then comes sample X with respectively 11668 $kN/m^2$ and 47.8% as strength and $CoV$. Sample Y has less strength but is the most trustful with 28.2% as $CoV$. For 10 min of mixing time, sample X has greater strength than samples Y and Z, but sample Y has the lowest $CoV$ and is more uniform in terms of strength distribution.

When one looks at the average values of the strength for the three samples for 10 min of mixing time, samples X and Y have strength more than 500 $kN/m^2$. So, if one considers the standard strength value in the range of 500-1000 $kN/m^2$, then samples X and Y are acceptable (fulfill the requirement), but only

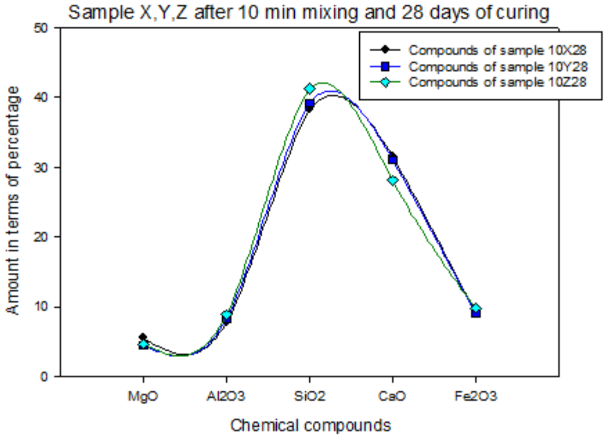

**Fig. 11 Sample X, Y and Z after 10 min of mixing and 28 days of curing times.**

sample Y is the most efficient because the strength inside is well distributed.

## 4. Discussion

From one side, we consider the main chemical components which are Silicon dioxide ($SiO_2$), Calcium oxide (CaO), Alumina ($Al_2O_3$), Iron oxide ($Fe_2O_3$) and magnesium oxide (MgO) in accordance with [7]. So, we assume that the strength of stabilized soil gradually increases with time, and there is transformation between the chemical elements especially with the calcium. The dissociated calcium ions ($Ca^{2+}$) react with the dissolved $SiO_2$ and $Al_2O_3$ from the clays particle's surface and form some chemical compounds. This point of view is not in contradiction with that of [8] for whom the strength increase of the improved soil is related to the dissolved silica and that the dissolution of the silica in clay minerals needs a long time.

The two chemical reaction processes such as primary cementing reactions and the secondary cementing reactions (pozzolanic reaction) are for the first one, due to the hydration between water and the four main constituents of cement which are the dicalcium silicate $[(CaO)_2SiO_2]$, tricalcium silicate $[(CaO)_3SiO_2]$, tricalcium aluminate $[(CaO)_3Al_2O_3]$, and the tetracalcium alumino-ferrite $[(CaO)_4Al_2O_3Fe_2O_3]$ [9]. For the pozzolanic reaction, the hydrous silica and alumina will gradually react with the calcium ions liberated from the hydrolysis of cement, to form insoluble compounds, which harden to stabilize the soil. That increases the strength and durability of the soil-cement by producing an additional cementing substance to further enhance the bond strength between the particle and are responsible of the increasing of CaO when the curing time become important like 28 days.

From the other side, if we deepen the discussion by trying to think about the mechanism of cement stabilized clay, cement mainly contains tricalcium silicate ($C_3S$), dicalcium silicate ($C_2S$), tricalcium aluminate ($C_3A$) and tetracalcium alumino-ferrite ($C_4AF$), which are the major strength development compounds. So, when the pore water of soil encounters with the cement, the major cement products and hydrated lime $Ca(OH)_2$ occur. The cement stabilized clay also induces pozzolanic reaction because the $Ca(OH)_2$ is produced after hydration and will dissolve the $SiO_2$ and $Al_2O_3$ from the clay particles. The reactions equations given in the next example are for the case of tricalcium silicate, one of the most important constituents of cement.

$$C_3S + H_2O \longrightarrow C_3SH_x + Ca(OH)_2, \text{(hydrated gel)} \quad (1)$$

This Eq. (1) gives the primary cementitious products. And then because of the following (2):

$$Ca(OH)_2 \longrightarrow Ca^{2+} + 2(OH^-) \quad (2)$$

we have (3):

$$Ca^{2+} + 2(OH^-) + SiO_2 \text{ (soil silica)} \longrightarrow CSH \quad (3)$$

$$Ca^{2+} + 2(OH^-) + Al_2O_3 \text{ (soil alumina)} \longrightarrow CAH \quad (4)$$

These Eqs. (3) and (4), by the pozzolanic reactions give the secondary cementitious products. And Fig. 7 shows that even though 1 hour and 2 hours of curing time are close. According to Fig. 8, one can conclude that having more curing time is better even though the mixing time of 1 min is not enough. That's why for 10 min of mixing time the tendencies of all the curves look closer for any curing time.

Additionally, to the same observations as the curves of sample X, we notice the sample Y that for the curve of 28 days of curing time it is different from all the rest for 1min of mixing. So, it means that 1 min of mixing time is not good, but it is attenuated when the time of curing becomes very long, such as 28 days. So, why for 10 min of mixing time all the curves look closer? Because the sample Y have the best conditions compare to the other sample.

From Figs. 9 and 10, in addition to some observations as the curves of samples X and Y which are same, we notice the sample Z that for the curve of 28 days of curing time it is different from all the rest for 1min of mixing, on the one side. And on the other side, the curves of 1 hour and 2 hours of curing time are close and the two others for 7 days and 14 days of curing time are also close. So, it means that 1 min of mixing time is not enough, that's why the curves are disparate. And for 10 min of mixing time, it is much better, and all the curves look the same in terms of tendency.

Fig. 11 shows that for 10 min of mixing time which is better than 1 min, sample X and Y curves are very close, but sample Z curve is a little bit off compared to the others. So, the reason for this gap is that Sample Z conditions are not good compared to the two others (particularly, because of the amount of cement).

So, finally with all these considerations and sharing the viewpoint of [6], the shear strength of cement stabilized soil gradually increases with time through pozzolanic reactions when CaO reacts with $SiO_2$ and $Al_2O_3$ in the soil. Additionally, it has been found that the greater the cement content is, the more stable is the sample and probably greater should be the strength of cement stabilized clay. And then, because water content is one of the main factors in cement stabilized clay, the strength development of cement stabilized clay decreases with the increase in water content according to some researchers, so that the cement content and the water content can be applied to predict the strength development of cement stabilized clay as proposed by [10]**.** However, what should be the strength distribution inside the columns for cement stabilized soft soil such as Ariake clay? Some researchers recommended W/C in the range of 0.6-0.8 [11] for soft marine clay of Singapore, or W/C = 1.0 for soft Bangkok clay [12]. Even, the same in the case of Ariake clay [3], but one still wonders if W/C = 1.0 is the most effective ground improvement specification to consider when performing cement deep mixing treatment on soft cohesive soil.

Although the reliability of NPI involves not only the distance between the measured points but also an assessment of the accuracy of the measurement process itself, as it is influenced by several disturbing factors such as excessive penetration forces or changes in penetration forces due to needle heating. However, an examination of the measured values allows us to safely state that there is an optimum value of W/C for which one can have not only an accepted strength but above all, a better distribution of that strength inside the soil-cement. As, if the strength distribution is uniform inside the soil-cement column, it better protects the infrastructure it supports against possible cracking due to the settlement of the parts of the column where the effect of the cement is absent.

## 5. Conclusion

This evaluation, which is both quantitative (percentage of determined chemical element) and qualitative (nature of the chemical elements making it possible to deduce the related chemical compounds) using X-Ray fluorescence, has made it possible to indicate through the chemical analysis that these three samples X, Y and Z of Ariake clay contain substantially the same chemical elements and mainly contain five (5) oxides namely silica or silicon oxide ($SiO_2$), alumina or aluminum oxide ($Al_2O_3$) and iron oxides or Ferric oxide ($Fe_2O_3$), Magnesia or magnesium oxide (MgO), and lime (more specifically quicklime) or calcium oxide (CaO). The X-ray fluorescence data analysis allowed us to identify, confirm and evaluate the minerals contained in the samples. The mineralogy of the soil-mixing materials tested depends on the mineralogy of the clays constituting the soil and the curing time, and for Ariake clay, on the water content and the cement dosage of the mixed material.

From this study one can conclude that the samples X and Y are much more stable and give good strengths that fulfill the range of 500-1000 kN/m$^2$, than the sample Z. According to the chemical components, especially the amount of silica and calcium oxide, one has good tendencies of its percentages for the ratio W/C = 1.0 and W/C = 1.5 after 10 min of mixing time when the curing time becomes important (28 days). The reason is that, the stability of the sample X and Y depends not only on the parameter W/C but also on the dosage of the stabilizer, the cement. Based on the investigations carried out the following conclusions are drawn.

As already known, the longer the mixing and curing time, the better the hardening conditions. W/C = 1.0 gives good strength (596 kN/m$^2$) to the soil when the amount of cement is C = 110 kg/m$^3$, and the $CoV$ is about 21%, which is acceptable. However, W/C = 1.5 shows better conditions with the same amount of cement, the strength is 539 kN/m$^2$ and $CoV$ is drastically reduce to about 15%. For W/C = 1.5 and C = 80 kg/m$^3$, the strength is very slow (384 kN/m$^2$) and non-well distributed with high $CoV$, more than 24%.

X-ray fluorescence does not make it possible to highlight the cement setting but combined with NPI, it gives a good idea about the quality of the mixture and therefore by the quantity of chemical components, and the strength distribution inside the soil sample, how is the hardening quality. By considering the chemical reactions which exist between all the components in the solidification of the soil-cement materials, one can state that when performing deep mixing treatment on soft cohesive soil such as Ariake clay, W/C = 1.0 is not the most effective ground improvement specification.

The contribution of this study in the field of DMM, is the perspective of the conditions by which there is an optimum value of W/C (W/C = 1.5) allowing to guarantee the required strength in the range of 500-1000 kN/m$^2$ and above all, gives an excellent distribution of the strength inside the soil-cement column.

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