

# Influence of Minor Elements in Clinker on the Properties of Cement: A New Approach for Application to Commercial Cement Manufacturing

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Cement manufacturers today use various waste materials and by-products as raw materials or fuels in cement manufacturing. Waste materials and by-products, however, often have certain chemical properties that differ from conventional raw materials and fuels. Thus, we have researched the overall influence of several minor elements in clinker on the properties of clinker and cement, and we suggest practical measures for Japanese cement manufacturers to take against the unfavorable influence of each minor element. This article introduces our approach and provides representative results and an example of commercialization. We also discuss further challenges in this field as it moves toward rational cement manufacturing.

Key words: Portland cement clinker, minor element, industrial waste, by-product, recycle.

## 1. INTRODUCTION

Consumption of waste materials and by-products used by cement manufacturers in Japan is currently increasing in order to demonstrate corporate social responsibility and achieve sustainable development through reduction of the final amount of waste disposal, while the domestic demand for cement decreases year after year, as seen in Fig. 1 [1]. According to the Japan Cement Association, Japan's cement industry is prolonging the remaining life of the final landfill sites for industrial waste by 1.5 years, while the actual remaining life is only 4.5 years [2]. The waste materials and by-products are used as alternative raw materials or fuels for clinker manufacture or as mixed materials for cement.

The reasons why cement plants can use waste materials and by-products are as follows [3]. First, all of the materials and fuels entering a cement plant are converted to product; the cement manufacturing process does not generate any new waste materials or by-products. Second, the cement manufacturing process, unlike other material processes raise the purity, does not require high-purity raw materials or fuels because cement is a mixture of hydraulic materials. Third, the raw materials are heated to 1723 K or more and converted to new hydraulic minerals in a rotary kiln that realizes a remarkably high temperature for a large-scale industrial process. Fourth, a large amount of the waste materials and by-products can be used since cement manufacturing is a typical mass production process.

Japanese cement manufacturers are increasing the export of their products due to a decrease in domestic demand. However, blended cement, e.g. Portland blast-furnace slag cement, is rarely exported. The cement manufacturers continue to satisfy the above-mentioned social role by increasing the use of waste materials and by-products as raw materials or

fuels for clinker manufacturing rather than for the cement mixture. Waste materials and by-products, however, often have certain chemical properties that differ from conventional raw materials and fuels used for clinker manufacture. The chemical properties of these materials must be carefully examined before use since they are closely related to the properties of the manufactured clinker and cement. We have researched the overall influence of several minor elements in clinker on the properties of clinker and cement, and we suggest practical measures to be taken by Japanese cement manufacturers against the unfavorable influence of each minor element [4 - 8].

This article introduces our approach to increasing the amount of alternative material consumption by Japanese cement manufacturers and provides representative results and an example of commercialization based on the obtained results. We also discuss further challenges to achieving rational cement manufacturing and

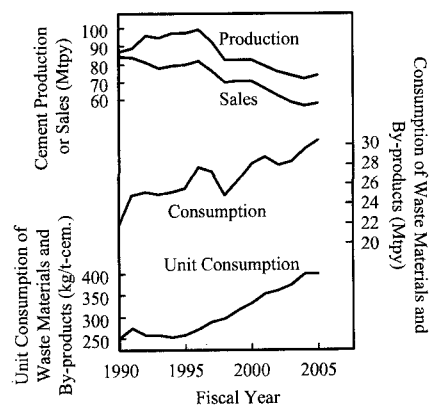


Fig. 1 Changes in production and sales of cement and the consumption and unit consumption of alternative raw materials and fuels by the Japanese cement industry [1].

sustainable development.

## 2. A NEW APPROACH TO THE EVALUATION OF MINOR ELEMENTS IN CLINKER

The influence or effect of the elements in clinker has already been investigated by a number of global cement chemists, with much important and basic knowledge now available [9]. However, cement manufacturers still need additional technological information to apply to practical manufacturing. The reasons are as follows.

First, it is necessary to consider the reality of the local cement market when evaluating the influence of minor elements on cement quality, since the required quality level of cement differs by region. For example, Japanese cement demanders require far higher quality than others, exceeding the specifications of the Japanese Industrial Standard. Japanese cement manufacturers should therefore abstain from directly applying the evaluation of a minor element in another region to the Japanese cement market. Second, much of the research provides only fragmentary information focusing on only some of the properties. In fact, the required cement capability is not a fragmented set of properties but rather a comprehensive set of properties, as illustrated in Fig. 2. Third, the previous research often evaluates the influence of minor elements qualitatively rather than quantitatively.

This ambiguity is caused by two main difficulties, namely the preparation of a sample and its evaluation. As for the former, sample cement that differs from the commercial product is often used; for the latter, a small-scale alternative technique is often applied. Clearly, it is not easy to prepare and evaluate samples, since this may require a large number of cement samples as well as special facilities, equipment, and techniques. We estimate that there are only a few research laboratories in Japan possessing the ability to prepare clinker and cement to an arbitrary specification and to then evaluate it using industrial testing.

We performed various investigations to evaluate the influence of minor elements using laboratory clinkers and cements corresponding to practical commercial cement, employing reliable industrial testing standards while taking into account the reality of the Japanese cement market. Although an actual plant trial will be required for a final practical investigation, we believe that our approach gives reliable results and saves time. This approach to investigating the influence of minor elements has lower risk and yields more intelligible

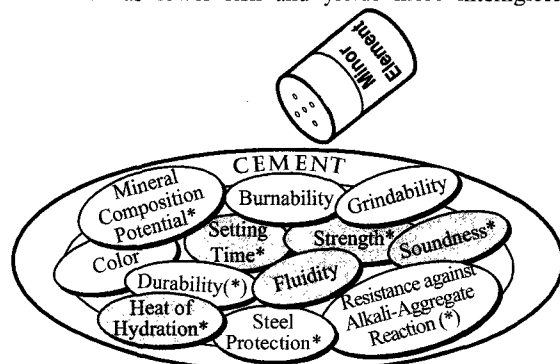


Fig. 2 Generally required properties of clinker and cement; \* and (\*) are directly and indirectly prescribed in JIS R 5210:2003, "Portland Cement."

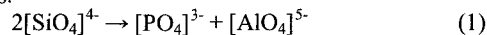
results than a trial at a cement plant, with its overly large production capacity and its tendency to vary a number of factors simultaneously. Moreover, if an unfavorable influence was found as a result of the evaluation, we would seek to establish a realistic countermeasure in the cement manufacturing process. Environmental friendliness must be made compatible with product quality. If the use of alternative materials causes a degradation of cement quality or imposes new limitations on cement users, we believe that the cement manufacturers must regard it as an undesirable approach.

## 3. OUTLINE OF RESEARCH RESULTS

### 3.1 Phosphorus Oxide ( $P_2O_5$ ) [5]

The "Waste Management and Public Cleansing Law" currently prohibits the ocean dumping of night soil, and will not permit the dumping of sewage sludge in Japan. Autonomies assuming responsibility for the final disposal of sewage sludge are currently searching for new final disposal sites. The chemical composition of dried sewage sludge is 15%  $SiO_2$ , 7%  $Al_2O_3$ , 3%  $Fe_2O_3$ , 3%  $CaO$ , and 6%  $P_2O_5$  and combustibles (3500 kcal/kg) [10]. These components are the same as typical cement raw materials, except for the  $P_2O_5$ . We researched the overall influence of  $P_2O_5$  in clinker on the properties of clinker and cement prepared in a laboratory using an electric furnace and a tube mill. In addition, disposal of animal waste containing  $P_2O_5$  has become a social problem since the Bovine Spongiform Encephalopathy (BSE) issue emerged in Japan in 2001. The results of our research can be applied not only to the use of sewage sludge but also to animal waste.

Alite, a major constituent contributing to the strength of Portland cement, decreased with an increase of  $P_2O_5$  in the clinker, finally disappearing at 4.8%  $P_2O_5$ . In contrast, the amount of belite and free lime (f.CaO) increased. The equilibrium calculation, a modified Bogue's calculation based on the phase diagram for the ternary system  $CaO - SiO_2 - P_2O_5$  [11], was sufficiently valid to predict variations in the mineral composition of clinker (Fig. 3). Moreover, the incorporation of phosphorus into belite, substituting silicon accompanied by aluminum [12] that was suggested by using an electron microprobe analyzer, was indirectly confirmed by comparing the predicted change in the amount of interstitial phases and the experimental change in the amount of residue from salicylic acid extraction, a precise chemical technique for extracting the interstitial phases.



The burnability and grindability of the clinker was degraded slightly with an increase of  $P_2O_5$  at  $P_2O_5$  levels of 2.0% or less, and were deteriorated immediately at 4.8%  $P_2O_5$ . The setting time was retarded at  $P_2O_5$  levels exceeding 2.0%, and compressive strength decreased for  $P_2O_5$  exceeding 1.0%. These undesirable influences were due to a decrease in alite and an increase in f.CaO. The compressive strength of cement containing 1.0%  $P_2O_5$  was nearly equal to that of 0.1%  $P_2O_5$ , with maximum compressive strength realized at 0.5%  $P_2O_5$ .

We determined the hydration ratio of alite in order to determine why the compressive strength was safely maintained at 1.0%  $P_2O_5$  despite a decrease in the alite amount. Fig. 4(a) depicts the hydration ratio of alite in cement fabricated from clinker of 0.1% and 1.0%  $P_2O_5$ .

The hydration ratio of the latter cement exceeded that of the former at each stage. Sichov reported higher hydraulic activity in synthetic tricalcium silicate containing P<sub>2</sub>O<sub>5</sub> [14]. It is reasonable to assume that the same phenomenon occurs in the alite of the cement. Here, the compressive strength of the cement is determined by the hydration amount, not by the hydration ratio. The hydration amount of alite can be represented by the product of the alite amount and the hydration ratio. The relationship between the compressive strength and the hydration amount of alite is illustrated in Fig. 4(b). The relationship is represented by a single curve regardless of the P<sub>2</sub>O<sub>5</sub> amount. Hence, the compressive strength of cement containing 1.0% P<sub>2</sub>O<sub>5</sub> is nearly equal to that of 0.1% P<sub>2</sub>O<sub>5</sub>, because of an increased hydraulic activity of alite in the cement at 1.0% P<sub>2</sub>O<sub>5</sub>.

As a conclusion of this research, we may state that the properties of cement are safely maintained at 1.0% or less P<sub>2</sub>O<sub>5</sub>. The undesirable influences of more than 1.0% P<sub>2</sub>O<sub>5</sub> are explained by a decrease in the alite amount and an increase in the f.CaO amount due to the change in the equilibrium state. Thus, there is no active measure against the unfavorable influence of P<sub>2</sub>O<sub>5</sub>. Cement manufacturers should maintain the quantitative relationship between CaO, SiO<sub>2</sub> and P<sub>2</sub>O<sub>5</sub> in raw materials, and not let the alite amount decrease excessively, referring to the phase diagram for the ternary system CaO - SiO<sub>2</sub> - P<sub>2</sub>O<sub>5</sub>. Generally speaking, the maximum amount of P<sub>2</sub>O<sub>5</sub> in clinker should be limited to 1.0%.

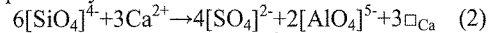
### 3.2 Sulfur Oxide (SO<sub>3</sub>) [4]

Petcoke is an oil refinery by-product obtained from the thermal decomposition of heavy oils. It often exhibits considerable sulfur content, but this does not result in high SO<sub>x</sub> emissions from the main stack of a cement plant because the increase in sulfur is incorporated into the clinker.

The influence of SO<sub>3</sub> on the properties of cement clinker and cement has been investigated in some countries outside of Japan. Previous researchers have reported that the influence of SO<sub>3</sub> in clinker depends on the amount of coexisting alkalis (Na<sub>2</sub>O and K<sub>2</sub>O) [9]. However, it is difficult to precisely control the amount of both SO<sub>3</sub> and alkalis because alkali sulfate tends to vaporize easily on burning. Due to this difficulty, there no research has been performed under conditions in which the amount of alkali was precisely fixed while the SO<sub>3</sub> amount was widely varied. Furthermore, the quantitative effects of gypsum and SO<sub>3</sub> in clinker have not been measured simultaneously despite a strong interest in the effect of adding gypsum along with an increase of SO<sub>3</sub> in clinker. Therefore, previous studies regarding the practical use of clinker with a large SO<sub>3</sub> amount are insufficient. In our study, the overall influence of SO<sub>3</sub> included in clinker on the properties of clinker and cement were investigated to satisfy the above conditions.

The amount of alite decreased with an increase in SO<sub>3</sub> amount in the clinker, while the amount of belite and interstitial phases increased. Fig. 5 presents a backscattered electron image and the distribution of calcium, sulfur, and potassium in clinker with 1.0% and 4.2% SO<sub>3</sub>. There were three types of SO<sub>3</sub> in the clinker:

alkali sulfate, anhydrite, and a solid solution of silicates. The mass balance of SO<sub>3</sub> in clinker can be obtained by considering the distribution of each phase. Sulfur was primarily incorporated into belite, replacing silicon accompanied by aluminum.



Here, Ca designates a cation (Ca<sup>2+</sup>) vacancy. A similar substitution was found in alite.

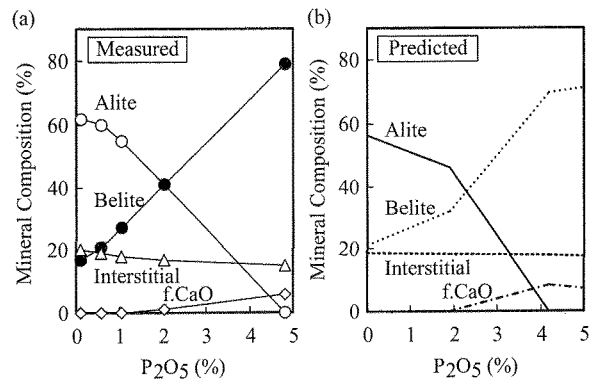
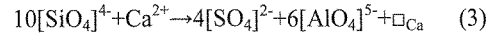


Fig. 3 Comparison of mineral composition between (a) as measured by the point-count procedure and (b) the predicted composition, based on the ternary phase diagram for the system CaO - SiO<sub>2</sub> - P<sub>2</sub>O<sub>5</sub>, after ref. [11].

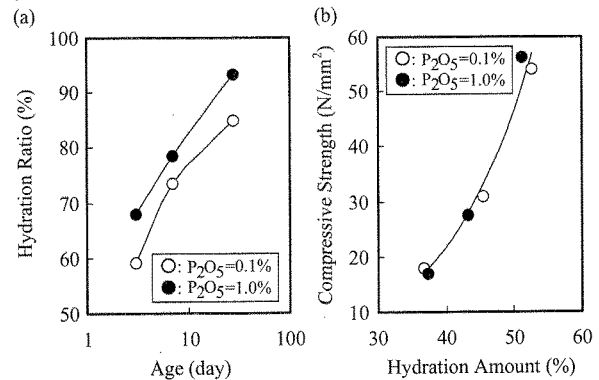


Fig. 4 (a) Variation in the hydration ratio of alite as a function of the material age, determined using a method from Ishizaki et al. [13], and (b) variation in compressive strength as a function of the hydration amount of alite, based on the hydration ratio and mineral composition as measured by the point-count procedure.

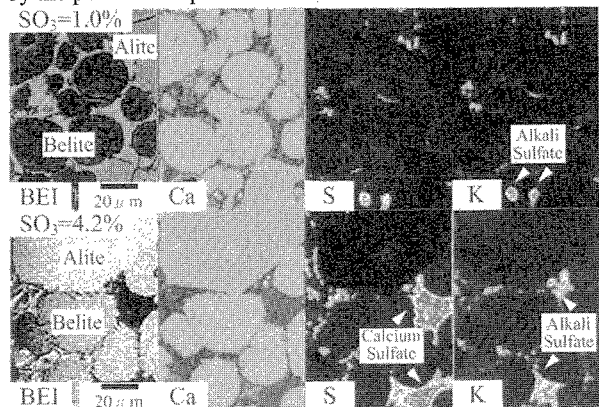


Fig. 5 Backscattered electron image and distribution of calcium, sulfur, and potassium in clinker at 1.0% and 4.2% SO<sub>3</sub>.

As for delayed ettringite formation (DEF), an expansive form of destruction that occurs after the hardening of concrete, we evaluated the risk of  $\text{SO}_3$  in clinker using the aluminum-to-sulfur ratio in silicates. The result was similar to that of Herfort et al. [15]. We determined that DEF is never caused by the hydration of high-sulfate silicates [16], even in the case of an extraordinarily large amount of  $\text{SO}_3$  in the clinker. In other words, DEF does relate to  $\text{SO}_3$  in concrete, but it will occur regardless of the amount of  $\text{SO}_3$  in the clinker.

The burnability of clinker was not affected by the amount of  $\text{SO}_3$ . However, the grindability was deteriorated as the  $\text{SO}_3$  increased. This was caused by densification of the clinker due to an increase in sulfates that form liquids during burning.

The setting time of the cement was slightly accelerated with increasing amounts of  $\text{SO}_3$  in the clinker, regardless of the amount of gypsum in the cement. However, the compressive strength depended on both the amount of gypsum in the cement and the amount of  $\text{SO}_3$  in the clinker. A portion of the  $\text{SO}_3$  in the clinker takes on the role played by gypsum in early hydration, and subsequently the  $\text{SO}_3$  in the clinker acts almost the same as gypsum. These relationships are explained by the amount of  $\text{SO}_3$  in the alkali sulfates and anhydrite that participate in early hydration and the amount of  $\text{SO}_3$  in the solid solution of belite that participates in the later hydration. Therefore, if the amount of gypsum in the cement is suitably reduced so that the compressive strength is kept constant in the early stage, the  $\text{SO}_3$  in the clinker exerts little influence on the later strength.

We concluded that the variation in cement properties is not very large while the variation in the clinker properties is remarkable. Changes in the properties of cement are avoidable with adjustments to the amount of added gypsum, i.e. by decreasing the added gypsum as the  $\text{SO}_3$  in the clinker increases. However, it should be noted that an excessive reduction in the amount of gypsum added might cause an extraordinary retardation of the concrete using a certain chemical admixture [17].

### 3.3 Manganese Oxide (MnO) [6]

Manganese is widely used as a material in batteries. The Drain Water Standard defines the concentration limit for manganese, although the Environmental Standard provides no prescription for Japan. Manganese is recovered from drain water from the plant and becomes concentrated in sludge. Moreover, various slags from ironworks contain manganese, although regular use of them is never observed because they lack the potential for hydraulicity found in blast furnace slag. Still, these slags have a potential for use as ferrous materials in cement manufacturing since they have a rather high iron content. The overall influence of manganese oxide on the properties of clinker and cement was investigated using laboratory clinker and cement. The maximum level of MnO found in clinker was 0.9%.

MnO improved the burnability of the clinker. The grindability of the clinker was

decreased slightly with an increase in MnO. The amount of ferrite increased and the amount of aluminates decreased with increasing MnO in the clinker. This variation essentially agreed with the estimate, assuming manganese behaves as a replacement for iron. The cement became dark blue in color following the addition of MnO (Fig. 6). The setting time of the cement was independent of the amount of MnO, despite the decreasing aluminates. Also, the compressive strength at ages of 3d and 7d was barely influenced by the amount of MnO. In contrast, the compressive strength at 28 days decreased with 0.4% or more MnO added (Fig. 7). The variations in the clinker and unhydrated cement properties can be explained by assuming that the MnO replaces iron in the clinker burning process. However, this assumption fails to explain the variations in the properties of hydrating and hydrated cement. These are adequately explained by the previous findings on the hydration of ferrite and the hydrate of alite. That is, manganese activates the hydration of ferrite [18] and alite [19] but degrades the strength of alite hydrate [19].

From the viewpoint of responsible cement manufacturing, the following guidelines, based on the amount of MnO, should be followed in order to avoid undesirable influence on the clinker and cement: (1) keep the total amount of manganese and iron constant, (2) modify the kiln burner operation to realize a slightly reducing atmosphere, and (3) modify the clinker modulus, including the hydraulic and the silica modulus.

### 3.4 Zinc Oxide (ZnO) [7]

The situation for zinc-containing waste and by-products is similar to that for manganese. The Drain Water Standard defines a concentration limit, although the Environmental Standard makes no prescription. Refining zinc produces a kind of non-ferrous slag as a by-product. These slags, which contain a high concentration of iron, are currently disposed of in landfills [20]. We investigated the overall influence of ZnO on the properties of clinker and cement.

Changes in the clinker phases were investigated using the point-count procedure, the salicylic acid - methanol extraction technique, and X-ray diffractometry (XRD). The ferrite and alite amounts increased and the aluminates amount decreased with increased ZnO in the clinker. As for the incorporation of ZnO into the clinker, an electron microprobe analysis clarified that zinc was incorporated into the clinker minerals by substituting for

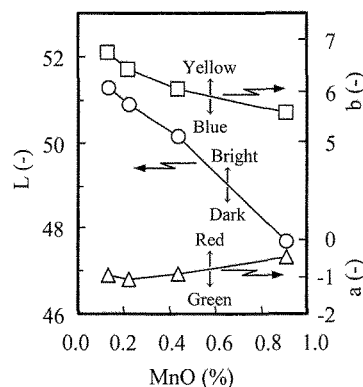


Fig. 6 Variations in cement color as a function of the MnO in clinker.

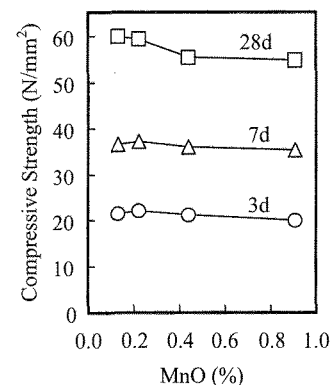


Fig. 7 Changes in compressive strength as a function of the MnO in clinker.

calcium. Furthermore, f.ZnO (free ZnO; zincite) was found by XRD at ZnO levels of 1.1% or more.

The burnability of the clinker under constant burning conditions was improved by ZnO. However, the grindability of the clinker, based on obtaining a constant specific surface area, was decreased with increasing ZnO, since this increased the amount of liquid phase in the clinker during the burning process.

The setting time (Fig. 8) was unchanged at ZnO levels of 1.1% or less. However, it was extraordinarily retarded at 2.2% due to excessive f.ZnO. The compressive strength (Fig. 9) at 3d and 7d increased with increasing ZnO except at a level of 2.2%, where early hardening was extraordinarily delayed by the f.ZnO. In contrast, the strength at 28 days increased with increasing ZnO, including at a level of 2.2%.

According to the above results, there is no influence on the properties of cement in the range where all the zinc is incorporated into the clinker minerals. The undesirable influence of ZnO on the cement properties is exemplified by the serious damage to early hardening due to f.ZnO, leading to retardation of setting and a decrease in early strength. It would be very difficult to prevent the undesirable influence of ZnO with an additional measure. Therefore, cement manufacturers must take sufficient care when considering the amount of ZnO in raw materials to ensure that all of the ZnO is incorporated into the clinker minerals, permitting a minimum amount of ZnO to form f.ZnO.

#### 4. AN EXAMPLE OF COMMERCIALIZATION [10]

The studies introduced in Section 3 are only the first step toward commercialization in actual cement plants. Some of the studies could lead to successful commercialization, but unfortunately the rest are unlikely to do so due to various obstacles. Furthermore, the concentrations of minor elements used commercially in cement plants are kept somewhat lower than laboratory results suggest in order to maintain the quality of the cement. We now introduce the use of sewage sludge in cement plants as an example of commercialization based on our research.

In 1997, Mitsubishi Materials Corporation began using sewage sludge for its cement manufacturing (Fig. 10). The sewage sludge is injected directly into the tail of the rotary kiln, that is, at the starting point for clinker burning, and safely combusted at a high temperature. This technology draws on not only the study on the

quality of cement and clinker introduced in Section 3.1 but also other studies on the receipt, injection and transportation of sewage sludge. In particular, an effective measure against the odor of sewage sludge was needed in order to achieve commercialization. This system is now being successfully applied at nine of the 32 cement plants in Japan, operated by a number of cement manufacturers. The use of sewage sludge also has an incidental environmental effect. Cement manufacturers must always pay attention to emissions of thermal  $\text{NO}_x$  since the burning temperature of a rotary kiln is remarkably high. The ammonia in sewage sludge denitrates approximately 40% of the  $\text{NO}_x$  from the kiln exhaust gas.

#### 5. FURTHER CHALLENGES

Researchers today are proposing various approaches to the use of alternative materials and fuels in order to encourage the cement industry to satisfy its social role [21]. With regard to minor elements in clinker, we expect the following studies to be required in the future.

First, there are some unresearched minor elements that are important in the management of cement plants. The influence of such elements on the properties of clinker and cement should be investigated as soon as possible. For example, the overall influence of calcium-replaceable elements should be clarified. A ton of clinker manufacture consumes approximately 1100 kilograms of limestone, and the total unit consumption of raw materials including limestone is 1550 kg/t-clinker. Today, Japanese cement manufacturers use alternative materials mainly substituting for sand, shale, or iron sources. Thus, the substitution of raw materials other than limestone is already reaching its limit. However, limestone, used most extensively in cement manufacturing, is rarely replaced because no calcium-rich alternative materials have been found despite the efforts of cement manufacturers. Substitution by an alternative material that contains calcium-replaceable elements like magnesium, strontium, or barium is considered to be the second-best approach. The practical influence of some of these elements has not been sufficiently clarified.

Second, the influence of minor elements simultaneously incorporated into clinker will be important in the future. In this study, we have discussed the influence of individual minor elements and the corresponding countermeasures. Minor elements

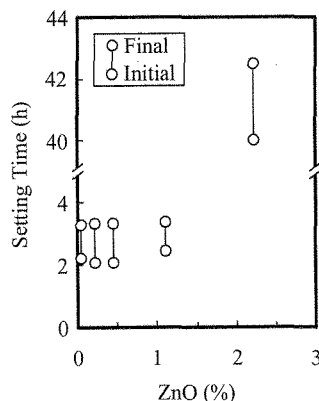


Fig. 8 Variation in setting time as a function of ZnO in clinker.

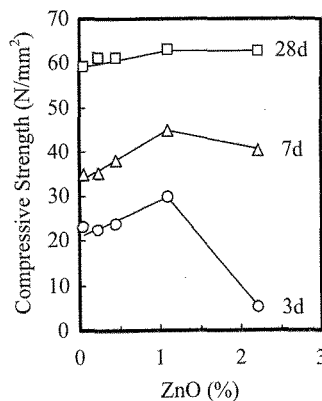


Fig. 9 Change in compressive strength as a function of ZnO in clinker.

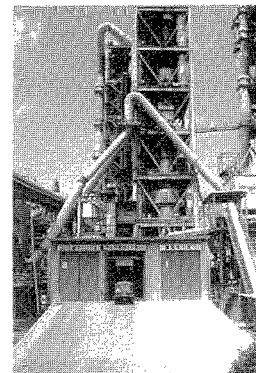


Fig. 10 The first sewage sludge receiving facility at a cement plant in Japan.

simultaneously incorporated into clinker will affect the properties of the cement synergistically or antagonistically, depending on the combination of minor elements. In particular, we expect to see control of the undesirable influence of a minor element exerted by other minor elements. For example, as described in Section 3.4, newly generated f.ZnO seriously damages the properties of cement. If we could shift the range of f.ZnO formation upward, the consumption limit for Zn-containing materials would be increased. This leads to the question of whether it is possible that adding another minor element would extend the limit on the amount of ZnO to the point where all of the ZnO is incorporated into the clinker minerals. We believe that this will be made possible by taking the ionic radius, the electric charges of the elements, and the tolerance of the crystal structures into account.

Throughout our research, we have noticed that elements in clinker behave complementarily in the clinker minerals. For example, the substituted incorporation of phosphorus or sulfur into the silicates accompanied by aluminum, previous Formulae (1) to (3) which are similar to Tschermak substitution, is rendered fairly understandable by taking into account the complementarities for the ionic radius, the number of atoms participating in the substitution, and the electric charge. The ionic radii of  $Al^{3+}$ ,  $Si^{4+}$ ,  $P^{5+}$  and  $S^{6+}$  are 53pm, 40pm, 31pm and 26pm [22].  $P^{5+}$  and  $S^{6+}$  are too small to substitute  $Si^{4+}$  independently. Therefore  $Al^{3+}$ , which is larger than  $Si^{4+}$ , complementarily accompanies  $P^{5+}$  or  $S^{6+}$  and stabilizes tetrahedral silicate anion,  $[SiO_4]^{4-}$ . According to Formulae (1) - (3), the mean ionic radii after the substitution are 42pm, 35pm and 42pm; these are almost equal to 40pm, the original radius before the substitution. The number of atoms participating in the substitution is held constant before and after the substitution in order to maintain the silicate anion structure. Of course, the electrical neutrality rule is always maintained in any substitution. Here it should be noted that the substitution is carried out in such a way that the anion structure is maintained even if a cation vacancy is introduced. This is evidence that a framework of silicate anions is especially important for the crystal structure of silicates. In addition, both the ionic radius change and the number of formed vacancies given by Formula (2) for belite are larger than those given by Formula (3) for alite. This means that the crystal structure of belite has a higher tolerance to guest elements than that of alite. This discussion presents a rather rough and limited story covering only silicate anions in silicates, but similar rules may be applied to other sites or clinker minerals. Further research demonstrating avoidance of the undesirable influence of one minor element through the use of another minor element is expected.

## 6. CONCLUSIONS

This article introduced our approach and provided representative results and an example of commercialization. Our overall and realistic approach to the properties of clinker and cement was successfully applied to the commercialization in cement plants; and this article also discussed further challenges to encourage the cement industry to satisfy its social role

including the application of Tschermak-type substitution in clinker phases.

Since Joseph Aspdin, a bricklayer in the pre-Victorian era, patented Portland cement in 1824, its name has never changed, but its manufacturing process and chemical composition have experienced continuous change. We believe that the participation in new experiences mentioned above is important for the cement industry expected to satisfy its social role effectively in the future.

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