

Development and Evolution of Soil improvement Materials, with Immobilizing Properties for Heavy Metals, Derived from Waste Gypsum Board

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Abstract

Gypsum board has been widely used as a building material due to its excellent fire resistance, soundproofing properties, and affordability. Reflecting its high production volume, however, the amount of waste gypsum board generated from building demolitions (hereinafter, referred to as waste gypsum board) has been increasing, raising concerns about the saturation of final disposal sites. Given this situation, the development of recycling technologies for waste gypsum boards has become an urgent necessity. The author and colleagues have developed equipment for producing bassanite and Type II anhydrous gypsum from waste gypsum board and have quickly brought it to market. In this paper, we focus on a soil improvement material, produced using the equipment, that has significant demand potential in civil engineering for bassanite and Type II anhydrous gypsum. We also trace the background and progress of our company's research and developments in this field. Specifically, we examine the effectiveness of bassanite, which sets upon hydration, as a soil improvement material for soft ground and mud. Additionally, we assess the effectiveness of bassanite as a solidification material that allows variation in the mixing ratio of bassanite and Type II anhydrous gypsum to adjust the setting time as needed. Furthermore, we have devised a composite recycling material that is based on bassanite derived from waste gypsum board, and combined in a ratio with coal ash and blast-furnace slag, which are rich in alumina and calcium oxide, to maximize the generation of ettringite chemically equivalent. Finally, we demonstrate that this composite recycling material is effective not only as a soil improvement material but also as an immobilizer for heavy-metal soil contaminants such as fluorine, hexavalent chromium, cadmium, lead, and arsenic.

Keywords: immobilizer for heavy metals, soil improvement material, ettringite, gypsum, coal ash, blast-furnace slag

1. Introduction

The development process and prospects of equipment for producing bassanite and Type II anhydrous gypsum from waste gypsum board have been detailed in the previously published Nikko Technical Report Vol. 1, No. 1, 2020, titled "Development of Equipment for Producing Bassanite and Type II Anhydrous Gypsum." This paper focuses on a soil improvement material, produced by the equipment, with significant demand potential in civil engineering for bassanite and Type II anhydrous gypsum, as well as a immobilizer for heavy metals, and traces the background and progress of the development.

In "2. Background," we provide an overview of the historical context leading to the widespread use of gypsum board as an interior material in buildings. It also reviews the legal regulations and their history concerning the disposal of gypsum board waste, which inevitably follows its widespread use, and examines the trends in

recycling waste gypsum board.

In "3. Types and Characteristics of Gypsum," we attempt to classify gypsum based on its origins and provide an overview of the classifications and their characteristics based on crystal structures which are essential to its nature as a material.

In "4. Soil Improvement Material Derived from Waste Gypsum Board," the focus is on the effectiveness of bassanite, manufactured from waste gypsum boards, as a soil improvement material and solidification material for muddy soil. The property of bassanite to set upon the addition of water (hydraulicity) is noted for its efficacy as a soil improvement material. However, if the setting is too rapid, it may adversely affect workability. Therefore, this study examines the possibility of adjusting the setting time to optimize workability by varying the mixing ratio of bassanite and Type II anhydrous gypsum.

In "5. Immobilizer Derived from Waste Gypsum

Board," we focus on the effectiveness of a composite recycling material that is based on the bassanite manufactured from waste gypsum boards, as an immobilizer for heavy metals. First, we highlight the effectiveness of ettringite in immobilizing heavy metals and note that the minerals constituting ettringite are alumina, calcium oxide, and calcium sulfate. We then devise a composite recycling material by optimally blending coal ash and blast-furnace slag, industrial by-products rich in these minerals, with bassanite from waste gypsum boards to maximize the production of ettringite in chemical equivalent. Furthermore, the composite recycling material is demonstrated to be not only effective as a soil improvement material but also highly effective as an immobilizer for heavy metals such as fluoride, hexavalent chromium, cadmium, lead, and arsenic, which are soil contaminants.

It should be noted that the details regarding the overview of the Soil Contamination Countermeasures Act, the purification methods, and the development history and prospects of soil purification plants at our company are reported in the previously published Nikko Technical Report Vol.4, No.1, 2023, titled "Development, Evolution, and Future Prospects of Energy-Saving Oil-Contaminated Soil Purification Plants."

2. Background

Gypsum board is known for its fire resistance, sound insulation, affordability, and excellent workability, and now widely used worldwide as an interior material for ceilings and walls in various buildings, including houses. In Japan, the rapid increase in the construction of new houses during the period of high economic growth, driven by a shortage of housing in suburban areas, led to the adoption of gypsum board as a replacement for Japanese traditional earthen walls, for wall and ceiling materials. Furthermore, modern Japanese houses have a lifespan of last about 30 years that is relatively short compared to that of general homes in Europe and the United States, due to the usage of various new building materials. Hence, the interval between construction and demolition is shorter, resulting in a higher output of waste gypsum board in Japan compared to Western countries.

Waste gypsum board, if mishandled, can produce toxic hydrogen sulfide, which causes a risk of leaching fluoride at levels exceeding soil environmental standards. Due to this risk, its disposal in controlled final disposal sites is strictly regulated by law. As a result, the remaining

capacity of these disposal sites in many municipalities is becoming strained, and disposal costs for waste gypsum boards are rising. Further, there is an increasing concern about illegal dumping. Considering these issues, there is a growing momentum for recycling waste gypsum boards as agricultural fertilizers or soil improvement materials.

In the following sections, the historical background of the widespread use of gypsum boards is overviewed, and the necessity for recycling waste gypsum boards is discussed from a regulatory perspective.

2.1 Historical Background

Triggered by the special demand from the U.S. military during the Korean War that broke out in 1950, Japan experienced a period of high economic growth exceeding an annual rate of 10% over 18 years from 1955 to 1973. Concurrently, modern Western lifestyle and culture in clothing, food, and housing began to rapidly permeate Japanese society, leading to the Westernization of Japanese living habits.

Secondary industries, particularly heavy and chemical industries with high productivity, started expanding rapidly in the Pacific Belt region in Japan, rather than primary industries such as agriculture and forestry. Business owners, facing a labor shortage, turned to rural areas for workers. Many laborers, who had been engaged in primary industries in rural and mountainous regions, migrated to urban areas in search of employment, prosperity, and convenience. Additionally, the trend toward nuclear families, driven by the desire to emulate Western lifestyles, led to a sharp increase in the number of households. This sudden growth highlighted the housing shortage in suburban areas, escalating into a social issue.

To address the housing shortage, the Japanese government rapidly promoted the construction of homes. These included culturally hybrid houses, combining Western and Japanese styles, and apartment complexes, sometimes disparagingly referred to as "rabbit hutches." To meet the high demand for timber due to this construction boom, the government implemented policies to actively promote the planting of fast-growing coniferous trees such as cedar and cypress. However, it takes decades for these trees to mature, resulting in the emergency importation of inexpensive timber from North America and Canada. At that time, no protective measures were taken for the domestic forestry industry, leading to a chronic fulfillment of domestic demand with cheap foreign timber. As a result, now-mature coniferous forests

are not used as building materials and instead release large amounts of pollen in spring, increasing the number of hay fever sufferers.

In terms of living environments, Western lifestyles, transitioning from tatami to chairs, became popular. Accordingly, housing structures and building materials, with new materials that were rational, practical, and economical, like gypsum board, as well as chemical materials and new construction methods, became preferred. Traditionally, Japanese architecture features a combination of tiled roofs and wooden structures with earthen walls and fittings made of wood and paper, harmonizing well with the seasonal climate changes and the practical aspects of daily life.

The earthen walls, a symbol of traditional Japanese houses, are constructed using a technique that involves multiple steps. The base layer consists of woven bamboo strips arranged in a grid pattern, called "takekomai." Over this, a mixture of clayey soil and straw (known as "susa") is kneaded with water and then applied by plasterers using trowels. However, this earthen wall technique declined with the onset of the high economic growth period, being replaced by the dry construction method using gypsum board.

Gypsum boards have significantly higher workability compared to earthen walls and can be easily cut with a saw or utility knife. It can be directly fastened, by nails for example, to inter-pillar beams and furring strips as core materials. Thereafter, applying wallpaper to the surfaces of gypsum boards results in an aesthetically pleasing wall finish.

Concurrently, the negative legacy of high economic growth became apparent as pollution emerged as a social issue. Keywords such as photochemical smog, acid rain, Yokkaichi asthma, Itai-Itai disease, and Minamata disease evoke the dire situations of that era. The deterioration of the living environment, known as the "Seven Typical Pollutions" including air pollution, water pollution, soil contamination, noise, vibration, land subsidence, and offensive odors, adversely affected public health. In response to this situation, the government finally made a belated break with its economic prioritization policy by passing 14 pollution control bills at the extraordinary Diet session of 1970, known as the "Pollution Diet."

Under the Air Pollution Control Act, emission standards for sulfur oxides and nitrogen oxides were tightened, leading to the installation of desulfurization

and denitrification equipment as flue gas purification devices at facilities generating smoke and soot. Inexpensive fuels such as coal and heavy oil contain high levels of sulfur, which, when burned, release sulfur oxides. Desulfurization equipment removes these sulfur oxides from flue gas through chemical reactions. There are various methods for removing sulfur oxides, and the most common is the lime-gypsum method which neutralizes sulfur oxides with lime (calcium carbonate: CaCO_3). In the neutralization, the sulfur oxides in the flue gas react with the lime, precipitating as flue-gas desulfurization gypsum (calcium sulfate dihydrate: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). This by-product, also known as chemical gypsum, has become a major raw material for gypsum board production.

It should be noted that limestone is a mineral resource that Japan can self-supply, with extensive deposits found throughout the country and in enormous quantities.

2.2 Resource Circulation of Waste

Japan has achieved high economic growth under a social system of mass production, mass consumption, and mass waste. For resource-poor Japan to continue to grow economically, it is now necessary to thoroughly implement the 3Rs of limited resources: Reduce, Reuse, and Recycle, and quickly build a recycling-oriented society.

According to statistics from the Ministry of the Environment for 1995, construction waste accounts for about 20% of the total industrial waste of 400 million tons, or 80 million tons, but construction waste accounts for more than 90% of the total illegally dumped industrial waste of 382,000 tons, or 353,000 tons. To solve this problem, the Law on Recycling of Materials Related to Construction Work, commonly known as the Construction Recycling Law, was enacted on May 31, 2000 (Heisei 12) as Law No. 104. This law designates four items as specific construction material waste: concrete blocks, asphalt-concrete blocks, construction wood, and iron scraps. Furthermore, the law requires that construction projects of a certain size or larger must recycle specific materials through segregated demolition. This promotes the suppression and reduction of construction waste generation, encourages the recycling and reuse of construction materials through segregated demolition, and provides a framework for monitoring whether proper disposal is being carried out.

Additionally, according to the statistics from the

Ministry of the Environment for 2020, marking 20 years since the enforcement of the Construction Recycling Act, the annual generation of specific construction material waste included 35 million tons of concrete debris, 25 million tons of asphalt concrete debris, and 5 million tons of construction waste wood. The recycling rates for these materials were high, with asphalt concrete debris at the highest of 99.5%, followed by concrete debris at 99.3%, and construction waste wood at 96.2%. Furthermore, in terms of the recycled uses for these materials, asphalt concrete blocks were reused as recycled aggregate and base course material, concrete blocks as base course material, and waste wood as fuel in the form of wood chips.

As segregated demolition became mandatory under the law, waste wood and waste gypsum board, which were previously minced and dismantled with heavy machinery and treated as mixed construction waste, began to be treated separately. As a result of segregated demolition, the amount of mixed construction waste that is ultimately left behind has started to decrease. However, there is no statistically organized information at present on how the waste is separated by intermediate processors and how it is transported to recycling facilities or final disposal sites, and the recycling rate is estimated to be only 63.2%.

According to the statistical data from the Gypsum Board Industry Association for 2022, the annual production of gypsum board reached 4 million tons in Japan. Correspondingly, waste gypsum board, which is the subject of study in this paper, generated from house demolitions exceeded 1.2 million tons annually, and it is predicted to eventually approach 4 million tons.

However, the amount of waste gypsum board, at 1.2 million tons, is only 1/30th of that of concrete block debris, and the recycling technology and utilization methods for waste gypsum board are still underdeveloped. Consequently, waste gypsum board has not been designated as a specific construction material waste. As a result, there is currently no legal mandate to recycle waste gypsum boards, causing the necessity of final disposal. This situation has led to a strain on controlled final disposal sites in many municipalities and raised concerns about the potential for increased illegal dumping due to rising disposal costs.

The necessity for disposal at these controlled final disposal sites is attributed to that the disposal method of waste gypsum boards is strictly regulated by the Waste Disposal and Public Cleansing Law (hereinafter referred

to as the Waste Disposal and Public Cleansing Law). The legal regulation stems from the fact that gypsum boards can be a source of toxic hydrogen sulfide (H_2S), which is generated by the decomposition of gypsum boards by sulfate-reducing bacteria present in the soil. It is known that hydrogen sulfide occurs when all of the following conditions are met: (1) the presence of sulfate-reducing bacteria, (2) the presence of water, (3) temperature of around 30°C , (4) anaerobic conditions without oxygen, and (5) the presence of cellulose and sugars, such as paper, that serve as a metabolic energy source for sulfate-reducing bacteria.

Given this background, the Waste Disposal Law requires waste gypsum boards to be disposed of in controlled final disposal sites. However, as part of the deregulation measure, a notification was issued by the Director of the Water Quality Bureau of the Environment Agency on July 16, 1998 (Heisei 10) (Environmental Water Quality Notice No. 299) for a relaxation of these regulations. Specifically, gypsum powder from which the paper has been removed can be disposed of in stable final disposal sites, similar to glass and ceramics. This is based on the finding that the removal of cellulose, which serves as a nutrient source for hydrogen sulfide-producing bacteria, eliminates any hydrogen sulfide generation. The separated paper is recycled by paper companies or incinerated.

The development of a new business model for the intermediate processing of waste gypsum boards is particularly noteworthy. This model capitalized on the lower final disposal costs associated with stable waste compared to controlled waste. The intermediate processing companies accept new construction scraps and segregated demolition products of gypsum board at the standard final disposal cost for controlled waste. They then profit by separating the paper from the gypsum and disposing of the gypsum as stable waste. To ensure profitability, various devices have been developed to effectively separate the paper and gypsum components of gypsum boards and installed in society.

However, this business model was popular among the intermediate processors only for a short time. A study conducted by the National Institute for Environmental Studies¹⁾ reveals that, even if gypsum powder is finally disposed of in a stable form, trace amounts of paper fiber (cellulose) and sugars used as adhesives remain, which serve as nutrient sources and generate toxic hydrogen sulfide. In response to this report, the Director of the

Waste and Recycling Policy Division, Minister's Secretariat of the Ministry of the Environment, issued Notice No. 060601001, dated June 1, 2006 (Heisei 18), entitled "Handling of waste gypsum boards from which the paper has been removed." This notice lifted the deregulation measure and tightened regulations again, requiring that even high-quality gypsum powder from which the paper has been removed be disposed of in a controlled form.

It is easy to imagine that the intermediate processors of waste gypsum boards, who had been making a profit from the difference between the disposal costs for managed and stable waste gypsum boards, were suddenly left without a viable business model. This led to the private sector taking the initiative to create a new business that would use the gypsum powder, produced by removing the paper from waste gypsum boards, as a recycled resource for other purposes.

The ideal way to recycle waste gypsum boards would be to reuse them as raw materials for new gypsum boards, i.e., "board to board." However, when considering the total amount of gypsum distributed, recycling them as raw materials for new gypsum boards would immediately result in a loss of a place for the flue gas desulfurization gypsum located upstream in the distribution. Therefore, it is necessary to create new uses to replace the "board to board" model. Gypsum is often used in familiar products such as chalk for writing utensils, white lines on playgrounds, and medical casts, but given that the annual amount generated is 1.2 million tons, it is more appropriate to recycle it into agricultural fertilizers and civil engineering materials, which are expected to have a large demand. In this case, attention must be paid to the generation of hydrogen sulfide and the leaching of fluorine.

Meanwhile, lime (calcium carbonate), which is abundant in Japan, can be used in the first stage as a neutralizing agent to remove sulfur oxides from combustion exhaust gas. In the second stage, flue gas desulfurization gypsum, which is produced as a by-product in the first stage, can be reused as a raw material for gypsum boards. In the third stage, the waste gypsum boards that have finished their role as building materials and are no longer needed can be reused again as agricultural fertilizer or civil engineering materials, finally returning to the soil. In this way, lime can be said to be an extremely useful domestic resource that can be used in a

cascade manner.

3. Types and Characteristics of Gypsum

This chapter provides an overview of the origin of gypsum formation and the classification based on differences in crystal structure, which is the essence of the substance, and provides an overview of gypsum and their characteristics.

3.1 Classification of Gypsum Formation by Origin

Based on the origin of its formation, gypsum can be broadly classified into "natural gypsum", "chemical gypsum" which is an artificial by-product, and "recycled gypsum" made from waste gypsum board.

3.1.1 Natural Gypsum

We need to track back to the ancient primitive Earth 4.6 billion years ago to know the origin of natural gypsum. The primitive Earth had violent volcanic activity thereover, releasing large amounts of sulfur dioxide gas, water vapor, carbon dioxide, and other gases along with volcanic smoke from the Earth's interior. The high-temperature, high-pressure atmosphere of up to 300 atmospheres did not contain oxygen (O₂), and was filled with 33% carbon dioxide (CO₂), nitrogen (N₂), water vapor (H₂O), sulfur dioxide gas (SO₂), and other gases.

As the earth began to cool, water vapor in the atmosphere condensed, and sulfurous acid gas dissolved in it, causing a large amount of sulfuric acid rain that eroded the earth. At that time, various minerals, including calcium, were dissolved from the earth and flowed into the ocean, where calcium ions (Ca²⁺) and sulfate ions (SO₄²⁻) in the minerals combined to precipitate gypsum dihydrate (CaSO₄·2H₂O). This gypsum dihydrate is believed to have sunk to the seafloor and formed a gypsum layer. Later, this layer was raised above ground due to crustal movement, thereby creating the veins of natural gypsum that we mine today.

3.1.2 Chemical Gypsum

Chemical gypsum is a by-product of a chemical manufacturing process. Examples of chemical gypsum include flue gas desulfurization gypsum, phosphate gypsum, titanic gypsum, and fluorogypsum.

Regarding flue gas desulfurization gypsum, sulfur oxides are removed from combustion exhaust gases from

thermal power plants and the like, using calcium carbonate (CaCO₃) or calcium hydroxide (Ca(OH)₂) as a neutralizing agent, and then gypsum dihydrate (CaSO₄·2H₂O) is produced as a neutralized product. Sulfur oxides are produced by burning the sulfur contained in fossil fuels such as coal and oil, and include sulfur monoxide (SO), sulfur dioxide (SO₂), sulfur trioxide (SO₃), and disulfur trioxide (S₂O₃), which are collectively called SO_x. These SO_x lead to air pollution such as acid rain and photochemical smog, and cause health damages such as Yokkaichi asthma, a pollution disease. For this reason, the Air Pollution Control Act strictly regulates the amount and concentration of sulfur oxides emitted from smoke-generating facilities.

Phosphogypsum and titanic gypsum are produced by isolating useful substances from phosphate rock and titanic ore, respectively, using sulfuric acid. Lime (CaCO₃) is then used to neutralize the isolated sulfuric acid (H₂SO₄), resulting in the formation of gypsum dihydrate (CaSO₄·2H₂O) as the neutralized product.

Fluorogypsum is made by extracting hydrofluoric acid (HF) and fluorine (F), the raw materials for fluoro resin, from fluorite (CaF₂) using sulfuric acid (H₂SO₄), where gypsum dihydrate (CaSO₄·2H₂O) is precipitated as the resulting neutralized product.

3.1.3 Recycled Gypsum

As mentioned above, with the enforcement of the Construction Recycling Law, buildings that meet certain requirements are required to undergo segregated demolition. In particular, gypsum board, which is extensively used as an interior material for houses, is recommended to be separated and dismantled according to the "Manual for On-site Separation and Dismantling of Waste Gypsum Board" issued by the Ministry of the Environment. The separated and dismantled waste gypsum board is then taken to intermediate processing companies, where paper and impurities are removed, and the board is crushed to turn into recycled gypsum.

As mentioned in Chapter 2, one possible use for these waste gypsum boards is to recycle them into gypsum boards, that is, to regenerate gypsum boards from waste gypsum boards. However, flue gas desulfurization gypsum, which is a chemical gypsum, accounts for nearly 60% of the raw material for gypsum boards, and of the 4 million tons of gypsum boards manufactured annually, 2.4 million tons are derived from chemical gypsum. This means that gypsum boards play an extremely important

role in adjusting the supply-demand balance as a receptacle of flue gas desulfurization gypsum, and are indispensable in the current industrial structure.

For these reasons, if waste gypsum boards are collected and recycled into new gypsum boards, the flue gas desulfurization gypsum from the upstream loses disposal options and quickly overflows. Hence, recycled gypsum from waste gypsum boards is expected to be reused as agricultural fertilizer and building and civil engineering materials, which are expected to have many demands other than gypsum board recycling.

When using recycled gypsum produced from waste gypsum boards as agricultural fertilizer or civil engineering materials, attention must be paid to the leaching of fluorine. This is because flue gas desulfurization gypsum, containing trace amounts of calcium fluoride (CaF₂), is used as the raw material for gypsum boards. At coal-fired thermal power plants, in particular, trace amounts of minerals such as fluorite (calcium fluoride) are mixed into the fuel coal. When burned, the coal decomposes to produce hydrofluoric acid (HF), which is mixed into the combustion exhaust gas. It is presumed that this is neutralized with lime along with sulfur oxides, thereby introducing trace amounts of calcium fluoride (CaF₂) into the flue gas desulfurization gypsum.

3.2 Classification of Gypsum by Crystal Structure²⁾

Gypsum can be broadly classified into three types based on the number of crystal waters: gypsum dihydrate (CaSO₄·2H₂O: calcium sulfate dihydrate), bassanite (CaSO₄·1/2H₂O: calcium sulfate 1/2 hydrate), and anhydrous gypsum (CaSO₄: calcium sulfate). Furthermore, based on the difference in crystal structure, bassanite can be classified into *α*-type and *β*-type, and anhydrous gypsum can be classified into type III, type II, and type I. Additionally, it has been confirmed that anhydrous gypsum type III exists in both *α*-type and *β*-type forms. Therefore, gypsum can be classified into seven types, considering the number of crystal waters and the difference in crystal structure.

3.2.1 Gypsum dihydrate (CaSO₄·2H₂O)²⁾

Gypsum dihydrate is stable in nature and features a needle-shaped crystal structure. It dissolves in some water but does not chemically react with it virtually. When this gypsum dihydrate is heated (dehydrated) at a temperature

controlled between 130 and 180°C, bassanite (calcium sulfate 1/2 hydrate) is produced. The thermochemical formula is shown in Formula (1):

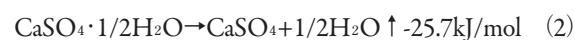


where the negative number on the right side indicates an endothermic reaction.

Regarding the fire resistance of gypsum, it should be noted that gypsum dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) containing 20.9% of its mass in water of crystallization is the base material for gypsum boards. When this water of crystallization is desorbed and evaporated, it absorbs a large amount of heat as shown in Formula (1), thereby preventing the temperature from rising and giving it excellent properties as a fire-resistant material.

3.2.2 Bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$)²⁾

Bassanite has the property of setting through a hydration reaction with water (hydraulic). As mentioned above, there are α -type and β -type bassanite s. The α -type has a dense structure with a high particle density and is stronger when hydrated than the β -type, therefore, it is used for medical casts for example. In contrast, the β -type has a smaller particle density due to its porous voids and is used as a building material, such as in gypsum boards. By heating either type of bassanite to 180°C or higher, anhydrous gypsum (calcium sulfate) is produced, with the crystal water removed. The thermochemical formula is shown in Formula (2).



3.2.3 Anhydrous Gypsum (CaSO_4)²⁾

Anhydrous gypsum is classified into three types: type III, type II, and type I. Type III is classified into α and β types, due to differences in crystal structure. Type III anhydrous gypsum is produced by heating gypsum in the range of 180 to 350°C, and it absorbs moisture from the air to return to bassanite. Type III anhydrous gypsum has a greater solubility in water than bassanite. Therefore, if Type III anhydrous gypsum is mixed with bassanite, the bassanite cannot convert to gypsum dihydrate until Type III anhydrous gypsum has completely converted to bassanite. Type II anhydrous gypsum is obtained by heating gypsum in the range of 350 to 1,000°C, and is also called inactive anhydrous gypsum because it does not return to bassanite even with hydration. Type I anhydrous gypsum can be generated by heating gypsum at 1,100°C or higher. Furthermore, if the temperature is increased

further under atmospheric pressure, it will thermally decompose into calcium oxide (CaO) and sulfur dioxide (SO_2).

4. Soil Improvement Material Derived from Waste Gypsum Board

In Section 1 of this chapter, recycled gypsum, produced by removing paper and foreign matter from waste gypsum board, is heated to produce bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and Type II anhydrite gypsum (CaSO_4). We then examine the hydraulic properties of these substances, which allow them to set with hydration, for their effectiveness as soil improvement materials. In Section 2, to address the handling issues caused by the extremely fast setting speed of bassanite, we focus on adding Type II anhydrite gypsum, which sets more slowly, and examine the relationship between the mixing ratio and setting speed to clarify the usefulness as a soil improvement material.

The samples of bassanite and Type II anhydrite gypsum used in the study in this chapter were produced using equipment for manufacturing bassanite and Type II anhydrite gypsum developed by the author and colleagues. The clay sample used was MC clay (kaolin), an industrial product with an adjusted composition. Furthermore, distilled water was used as the mixing water for the test specimens, as distilled water is thought to have the least difference in quality that affects strength development.

4.1 Effectiveness of Bassanite Produced from Recycled Gypsum as Soil Improvement Material

In this section, to verify the effectiveness of bassanite produced from recycled gypsum as a soil improvement material, bassanite was applied to cement-stabilized soil. Bassanite sets within a few minutes after hydration and exhibits high water absorption, making it potentially effective for application to muddy soil with high water content. Therefore, with an eye towards its applicability to clayey soil with high water content, uniaxial compression tests were conducted on two types of clay with water contents adjusted to 120% and 140%. The geotechnical significance of bassanite in these conditions was examined. Previous researches on this topic includes a study report by Kamei et al.³⁾⁴⁾

In this case, blast-furnace slag cement type B (JIS R 5210) was used as the stabilizer for its strength

characteristics and economic efficiency.

4.1.1 Preparation of Specimens and Experiment

In the experiments described in this section, specimens of cement-stabilized soil were prepared according to a specimen preparation method⁵⁾ that does not involve compaction of the stabilized soil. This method aims to improve clayey soils with high water content which require the addition of large amounts of stabilizers.

Assuming the stabilization of soft clayey soils with water contents of 120% and 140%, the mix conditions were set with two types of water content (a W/S ratio, where W is water, and S is soil mass) of 120% and 140% and a cement content (a C/S ratio, where C is cement) of 10%. Further, we considered whether the soil used in this study could be cast into a mold when bassanite was mixed in the subject soil. We set five mixes for the W/S ratio of 120% (0%, 5%, 10%, 15%, and 20%) and five mixes for the W/S ratio of 140% (0%, 10%, 20%, 30%, and 40%).

The specimens were prepared by adding mixing water and cement to MC clay (i.e., a clay sample) to achieve a specified moisture content, and then mixing with bassanite by a mixer to uniformly disperse the bassanite.

The completed specimens were subjected to measurement of water content and wet density, and then cast into a cast iron mold (ϕ of 50 mm, H of 100 mm). The specimens were covered with polyethylene bags to prevent drying after being cast into the mold, and cured in a temperature-controlled room ($20 \pm 2^\circ\text{C}$) for 24 hours. After 24 hours, the specimens were removed from the mold, placed in polyethylene cases, and cured in air in a temperature-controlled room ($20 \pm 2^\circ\text{C}$) for a specified curing period (i.e., 28 days). After the specified curing period, the specimens were subjected to uniaxial compressive strength tests.

4.1.2 Experimental Results and Discussion

Typical stress-strain curves for various bassanite mixing ratios (a B/S ratio) are shown in **Figures 1**⁶⁾ and **2**⁶⁾. **Figure 1** shows the case with a W/S ratio of 120%, while **Figure 2** with a W/S ratio of 140%. At both B/S ratios, the stress value shows a significant rise with increasing axial strain. Examining the stress-strain curve at a B/S ratio of 0%, in the case with a W/S of 120%, the stress value reached a peak of 230 kN/m² at an axial strain of about 1.5%, and decreased rapidly when the axial strain exceeds about 2.0%. Even in the case with a W/S ratio of

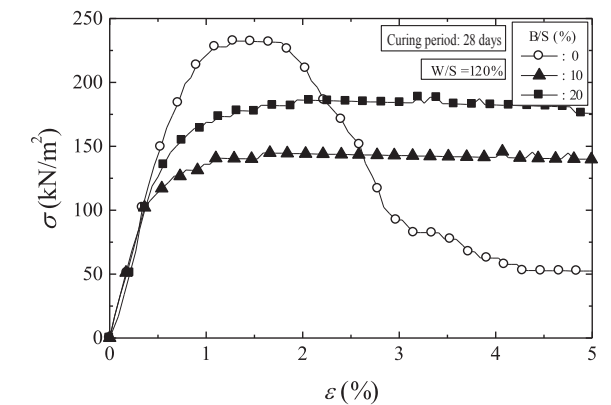


Figure 1: W/S ratio of 120%
Stress-strain curve for bassanite mixing ratio⁶⁾

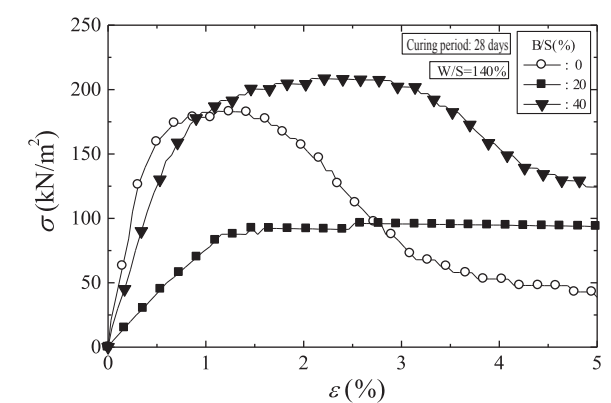


Figure 2: W/S ratio of 140%
Stress-strain curve for bassanite mixing ratio⁶⁾

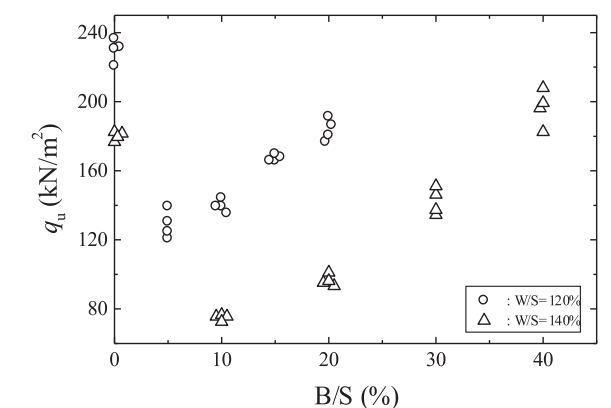


Figure 3: Relationship between uniaxial compressive strength and bassanite mixing ratio⁶⁾

140%, the stress value shows a tendency to decrease rapidly after reaching a peak of 180 kN/m² at an axial strain of about 1.0%.

When focusing on the stress-strain curves when bassanite was mixed, no clear peak was observed in the stress value. In the case with a W/S ratio of 140% and a B/S ratio of 40%, a decrease in the stress value was observed when the axial strain exceeded 3.0%. In the samples with other B/S ratios, however, even after the stress value reached its maximum value, the value did not decrease with increasing axial strain. This suggests that the

toughness of the ground increased and its durability became higher. In other words, it verifies that the mixing of bassanite provided viscosity to the ground material. In terms of the viscosity, it is considered that there is a close relationship between the amount of bassanite and the formation of ettringite (that is, as the amount of bassanite increases, the formation of ettringite increases).

Next, regarding the magnitude of the unconfined compressive strength (q_u), with a small B/S ratio, the q_u value was lower than in the case where only cement was added (a B/S ratio of 0%). However, when bassanite was added, the q_u value increased with an increase in the B/S ratio. The case with a W/S ratio of 140% and a B/S ratio of 40% was found to exhibit a higher value q_u than the case with only cement added.

Figure 3⁶⁾ depicts the relationship between the value q_u and the B/S ratio for clarification thereof. Regardless of the difference in W/S ratios, in cases with a B/S ratio of about 5 to 10%, the value q_u dropped sharply compared to the case with a B/S ratio of 0%. However, at higher B/S ratios, the value q_u is found to increase almost linearly. In particular, at a W/S ratio of 140%, the value q_u at a B/S ratio of 40% increased to about 1.1 times the q_u value at a B/S ratio of 0%.

The above results suggest that, to stabilize soft ground, a mixture of a small amount of bassanite limits the increase in strength due to cement, but that mixing more bassanite can improve the value q_u efficiently. Furthermore, gypsum having high water absorption is likely to be strengthened by the decrease in free water as the B/S ratio increases. The results of this experiment indicate that we are able to obtain a higher value q_u at higher B/S ratios, especially for clayey soils with high water content. Meanwhile, the results of previous experiments using bassanite produced by other processing methods also showed a tendency for higher values q_u along with higher B/S ratios³⁾⁴⁾.

The main factor of the strength reduction caused by the mixing of bassanite may be the inhibition of hydration reaction of the cement by the inclusion of gypsum. One of the clinker minerals that constitutes cement is the aluminate phase (C_3A), which reacts rapidly with water and instantly releases a large amount of heat to cure. Generally, gypsum is added as a set retarder in a cement manufacturing process to decrease the heat of hydration of the aluminate phase⁷⁾. We presume that the bassanite mixed in the study in this section also acted as a set retarder as used in the cement manufacturing process,

excessively limiting the setting of the aluminate phase and causing the strength reduction. One countermeasure is possible to this reduction in unconfined compressive strength, in which the amount of aluminate phase in the cement used is reduced, for example, by using sulfate-resistant Portland cement with a reduced amount of aluminate phase.

The above results indicate that, when preparing cement-stabilized soil, the bassanite absorbs water and turns into gypsum dihydrate, resulting in a decrease in the free water. We also assumed that as the B/S ratio increases, the free water decreases through this mechanism, and as a result, the strength increases. Therefore, we can say that bassanite produced from recycled gypsum is highly effective in improving soft ground with high water content, as it can consume large amounts of waste gypsum, which will lead to the resolution of the waste gypsum disposal problem. The bassanite produced from recycled gypsum is also significant from a geotechnical engineering perspective in that the strength of soft ground can be increased as the mixing rate increases.

4.2 Soil Improvement Material with Adjustable Setting Time

In a study⁹⁾ investigating the application of bassanite produced by heat-treating recycled gypsum to soft ground, significance was observed in that the rapid-setting rate of bassanite significantly enhances early trafficability. However, if the setting rate of bassanite is extremely fast, it may impede workability. To address this issue, in this section, focusing on the fact that the hydration reaction rate of Type II anhydrite gypsum is slower than that of bassanite, we examined the relationship between the setting time of MC clay (kaolin) that resembles soft ground by changing the mixture ratio of bassanite derived from recycled gypsum and Type II anhydrite gypsum, and verified its effectiveness of the mixture as a soil improvement material.

4.2.1 Preparation of Specimens and Experiments

In the experiment in this section, assuming that bassanite is used as a soil solidification material for soft ground with high water content, 50g of MC clay was hydrated to adjust the water content to four different water content ratios: W/S ratios of 120%, 140%, 160%, and 180%. Distilled water with a temperature of $15 \pm 2^\circ\text{C}$

was used for hydration due to its little effect on the pH of the sample or the mixed ions. The state of the sample adjusted to a W/S ratio of 140% is shown in **Photo 1⁸⁾**. For the samples adjusted to each of the water content ratios, the mixture ratios B/S were set to be 10%, 20%, and 40%.

Next, the mixture ratios A/B (A is anhydrite (type II anhydrite gypsum)) were set at 0%, 10%, 20%, and 40%. This was done to examine the relationship between the mixing ratio of bassanite, which has a fast setting time, and Type II anhydrite gypsum, which has a slow setting time, and their combined setting time. Additionally, 50 g of MC clay samples were prepared by adjusting the water content to five different values: W/S ratios of 100%, 120%, 140%, 160%, and 180%. For these five samples, the added amount (A + B)/S was determined to be 10%.

To evaluate the setting time, we need to adopt an index that facilitates immediate assessment. **Table 1⁸⁾** provides the indexes the author and colleagues devised in this experiment in this section for easy evaluation of the samples' setting time. We created these because the setting time of bassanite is often completed within a few minutes to a few tens of minutes and the time-requirement measurements, such as uniaxial compression tests, are inappropriate for this sample adjustments and setting-degree evaluation. We believe that our indexes can be applied to measure the setting time of bassanite for relative comparison between the setting times for the B/S ratios of 10%, 20%, 40%, and the A/B ratios of 0%, 10%, 20%, 40%, which fall within the range of this study. To avoid personal differences, a single person conducted all measurements.

The experiment in this section was conducted in a room with a controlled temperature of $20 \pm 2^\circ\text{C}$. Bassanite and a mixture of bassanite and Type II anhydrite gypsum were added to samples with adjusted moisture content. The samples were stirred with a laboratory spoon for 30 seconds. The setting time was determined as the time it took for the sample to reach level 3 on the index, "moist and breakable by hand." This was assessed visually and by hand inspection every minute. Level 3 was chosen as the standard for setting time judgment in this study because it represents a state where setting can be clearly judged through visual and tactile inspection, and it allows for quicker evaluations compared to levels 4 and 5.

In the study presented in this section, we focused on whether it is possible to adjust the setting time as desired



Photo 1: MC clay, at a W/S ratio of 140%, used in the experiment in this section⁸⁾

Table 1: Evaluation of setting time applied in the experiment in this section⁸⁾

Setting Index	Setting State of Sample
Level 1	fluid
Level 2	no fluidity, but rich in water and easy to dissolve
Level 3	moist and breakable by hand
Level 4	deformable slightly when pressed with fingers
Level 5	not deformable when pressed with fingers

by changing the mixing ratio of bassanite and type II anhydrous gypsum. Therefore, we did not add cements which could be a disturbing factor.

4.2.2 Experimental Results and Discussion (1) Relationship between B/S ratio (%) and Setting Time for Each W/S ratio (%) **Figure 4⁸⁾**

shows the results of the experiment conducted to examine the effects of varying bassanite addition ratios (B/S ratios of 10%, 20%, 40%) on the setting time of MC clay for soft ground (W/S ratios of 120%, 140%, 160%, 180%). Three tests were conducted for each mixture, and the results are plotted in the figure. **Figure 4** indicates that, for the bassanite addition ratio B/S of 10%, the setting occurred within 20 minutes at W/S ratios of 120% to 140%, but it took 50 minutes to set at a W/S ratio of 180%. For B/S ratios of 20% and 40%, the setting occurred within about 20 minutes at both water contents. Regarding the effect of differences in B/S ratios on setting time, a tendency was observed where the plots on the graphs shifted downward as the B/S ratio increased for all W/S ratios (%).

Figure 5⁸⁾ shows the effect of varying water content (W/S ratios of 120%, 140%, 160%, 180%) on the setting time for each bassanite addition ratio (B/S ratios of 10%, 20%, 40%). The figure clearly indicates that, at a W/S ratio of 120%, the setting took less than 5 minutes. However, as the W/S ratios increased, the setting time for each B/S ratio (%) increased exponentially. Specifically, at a W/S ratio of 180%, the setting time was 5 minutes at a

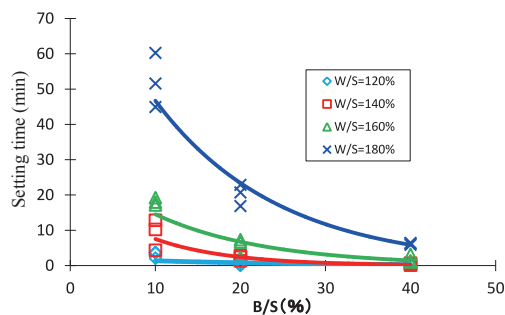


Figure 4: Effects of B/S ratios (%) at each W/S ratio (%) on setting time of soft clay⁸⁾

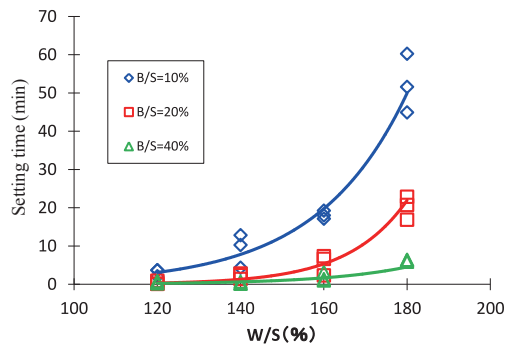


Figure 5: Effects of W/S ratios (%) at each B/S ratio (%) on setting time of soft clay⁸⁾

Table 2: Gypsum solubility⁸⁾

Temperature (°C)	Gypsum dihydrate (g/L)	Bassanite (g/L)	Type III Anhydrous gypsum (g/L)	Type II Anhydrous gypsum (g/L)
0	1.756	10.919	11.721	3.793
10	1.934	9.494	10.182	3.313
20	2.047	8.198	8.789	2.879
30	2.104	7.024	7.508	2.486
40	2.115	5.965	6.362	2.134

B/S ratio of 40%, 20 minutes at a B/S ratio of 20%, and 50 minutes at a B/S ratio of 10%. For all bassanite addition ratios, there is a tendency for the setting time to be significantly longer for W/S ratios of 140% and higher.

Researches on the setting mechanism of bassanite have been known for a long time¹⁰⁻²⁶⁾. Among them, Daimon et al.¹⁸⁾ clarified the mechanism of the qualitative relationship between the solubility and dissolution rate of bassanite, and the solubility and nucleation of gypsum dihydrate crystal growth. As for a study on delaying the setting time of bassanite¹⁹⁾, Yamada et al. confirmed that the dissolution rate of bassanite and the crystallization rate of gypsum dihydrate were reduced by adding sodium citrate or sodium acetate as a setting retarder. Other

setting retarders known to be effective for bassanite include organic materials such as gum arabic, gelatin, and starch, and inorganic materials such as borax and sodium phosphate.

To examine the process by which the bassanite produced from recycled gypsum used in the study in this section undergoes a hydration reaction and sets in high-water content MC clay that resembles a soft ground, we focus on the difference in solubility between gypsum dihydrate and bassanite, and make the following consideration.

Table 2⁸⁾ shows the results of calculations using the formula²⁰⁾ for gypsum solubility that has been proposed by Adachi et al. in a previous study. The table lists the solubilities (g/L) of, from the left, gypsum dihydrate, bassanite, Type III anhydrous gypsum, and Type II anhydrous gypsum at each temperature. Table 2 shows that the solubility of gypsum dihydrate at 10°C is 1.934g/L while that of bassanite is 9.494g/L. Therefore, the solubility of bassanite is nearly five times that of gypsum dihydrate. Since bassanite, i.e., calcium sulfate 1/2 hydrate (CaSO₄·1/2H₂O), is a sulfate, some of it is thought to dissolve in water and ionize into calcium ions (Ca²⁺) and sulfate ions (SO₄²⁻). When bassanite is abundant in the solvent water, in accordance with the dissolution rate of bassanite eventually, calcium ions reach a state of saturation.

For gypsum dihydrate, which has a solubility one-fifth that of bassanite, it is easy to assume that calcium ions are already in a supersaturated state. Supersaturated calcium ions take up the water of crystallization and crystallize gypsum dihydrate, i.e., calcium sulfate dihydrate (CaSO₄·2H₂O). This small amount of gypsum dihydrate is believed to act as a nucleation site, accelerating the precipitation rate of gypsum dihydrate in a chain reaction. When gypsum dihydrate is heat-treated to produce bassanite, a significant amount of gypsum dihydrate remains in the bassanite of low yield. This is because the lower the yield, the faster the setting of the bassanite, as the gypsum dihydrate acts as a nucleation site.

In parallel, the amount of gypsum dihydrate precipitates increases, reducing the calcium ions in the solution. Consequently, the solution transitions from a supersaturated state to an unsaturated state. The dissolution of bassanite continues as these mechanisms repeat. It is believed that bassanite is converted to gypsum dihydrate through this hydration reaction process.

Based on the above description, it can be easily inferred that, for the samples with high water content as shown in Figure 4⁸⁾ and Figure 5⁸⁾, the time until bassanite dissolves to make the solution supersaturated is longer than those of samples with low water content. Therefore, the lower the water content of the sample, the faster the reaction and the faster the setting of the sample, so that gypsum dihydrate precipitates after calcium ions become supersaturated.

(2) Relationship between A/B ratio (%) and Setting Time for W/S ratio (%) and Discussion⁸⁾

Figure 6⁸⁾ shows the results of the experiment conducted to investigate the effect of various mixture ratios (A/B) (%) of Type II anhydrite gypsum and bassanite on setting time. The addition rate of the mixture (bassanite and Type II anhydrite gypsum) to the sample was determined to be 10% ((A + B) / S) · 100 = 10%). This rate was chosen because we considered that it would most significantly affect the setting time in relation to differences in water content, similar to the relationship between B/S ratios (%) and the setting time for each W/S ratio (%) examined in Section (1). As in Section (1), three tests were conducted for each mixture, and the results are shown in the figure.

In the figure, no delay in setting was observed for the W/S ratios of 100% and 120% even as the A/B ratios (%) increased. This result is likely due to the water content values at W/S ratios of 100% and 120% being lower than those of the other samples, resulting in a smaller amount of water used as the solvent. Therefore, even with a small mixing ratio of bassanite, the time until the concentration of dissolved calcium ions reached saturation was short. Conversely, when comparing samples with higher water-content values from the perspective of gypsum dihydrate solubility, it is inferred that the time until the calcium ion concentration reaches supersaturation is shorter for samples with low water content than for those with high water content, which accelerates the crystal precipitation of gypsum dihydrate. For these reasons, the effectiveness of Type II anhydrite gypsum as a setting retarder is not observed in the range of W/S ratios of 120% or less, where the water content is low in the study in this section.

As for the higher water-content samples with W/S ratios of 140-180% shown in the figure, it is clear that the setting time increased as the A/B (%) value increased.

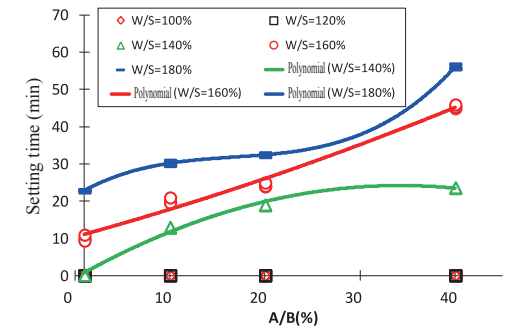


Figure 6: Effects of A/B ratios (%) at each W/S ratio (%) on setting time of soft clay⁸⁾

Specifically, at a W/S ratio of 180%, the setting time increased sharply for an A/B ratio of 40%. For a W/S ratio of 160%, the A/B ratio (%) and the setting time were in a proportional relationship. Furthermore, when comparing the solubility of bassanite and Type II anhydrite gypsum at a dissolution temperature of 10°C (from Table 2⁸⁾), bassanite was 9.494 g/L, while Type II anhydrite gypsum was 3.313 g/L, which is about one-third less. Additionally, the solubility of gypsum dihydrate at the temperature was 1.934 g/L. Therefore, the solubility values are in the order of bassanite > Type II anhydrite gypsum > gypsum dihydrate.

Based on these findings, it is inferred that the calcium ion concentration in the solvent during the crystal precipitation of gypsum dihydrate is controlled not only by bassanite but also by Type II anhydrite gypsum, with respect to the solvent that is abundant in the higher water-content sample.

The setting mechanism of gypsum dihydrate is believed to proceed with trace amounts of gypsum dihydrate acting as nucleation sites, leading to the precipitation and growth of needle-like gypsum dihydrate crystals. Since the solubility of gypsum dihydrate is approximately one-fifth that of bassanite, it is thought that the precipitation process continues until all the bassanite is dissolved and the calcium ion concentration in the solvent is reduced to about one-fifth or less.

The solubility of Type II anhydrite gypsum is about one-third that of bassanite. Therefore, it is considered that the dissolution of Type II anhydrite gypsum begins after the dissolution of bassanite is completed and the calcium ion concentration in the solvent drops to about one-third or less. Based on this consideration, the larger the A/B (%) value of the sample, the more the calcium ion concentration is controlled by the dissolution rate of Type II anhydrite gypsum after the dissolution of bassanite is completed, and the longer it takes for the calcium ion

concentration to become supersaturated from the perspective of gypsum dihydrate. For these reasons, the setting time is believed to be delayed as the A/B (%) value increases. As is clear from **Figure 6**⁸⁾, this is more pronounced as the W/S ratio (%) increases, and the setting time is exponentially long at a W/S ratio of 180%.

Furthermore, **Table 2**⁸⁾ shows that the solubility of Type III anhydrite gypsum at 10°C is 10.182 g/L, which is greater than that of bassanite, 9.494 g/L. From these results, it is presumed that by increasing the amount of Type III anhydrite gypsum added, the calcium ion concentration in the solvent increases further and the precipitation rate of gypsum dihydrate increases. Therefore, the following is suggested: to decelerate the setting of bassanite, we can increase the amount of Type II anhydrite gypsum to add, and to accelerate the setting of bassanite, we can increase the amount of Type III anhydrite gypsum to add, which enables an extensive range of adjustment of the setting time as desired.

Also, **Table 2**⁸⁾ shows that the solubility of gypsum dihydrate increased as the temperature of the solvent increased. However, the solubilities of bassanite, Type III anhydrite gypsum, and Type II anhydrite gypsum tended to decrease as the temperature of the solvent increased. This is thought to be due to the fact that both the thermochemical equation (1) from gypsum dihydrate to bassanite mentioned in ‘3.2.1 Gypsum Dihydrate’ where dihydrate gypsum becomes bassanite and the thermochemical equation (2) mentioned in ‘3.2.2 Bassanite’ where bassanite becomes anhydrous gypsum are endothermic reactions. These support the fact that the lower the temperature, the faster the setting of bassanite, Type III anhydrous gypsum, and type II anhydrous gypsum after hydration.

The above examination revealed that the setting time can be controlled as desired by changing the mixing ratio of bassanite and type II anhydrous gypsum. Therefore, it is expected that the use of the mixture as a soil improvement material will be further expanded, such as in deep mixing, where water is added to a solidification material to make it into a slurry and then pumped. This was not traditionally possible due to the short setting time of solidification materials using bassanite as a base material.

5. Immobilizer Derived from Waste Gypsum Boards

In a previous study³³⁾, the author and colleagues investigated a composite recycled material made by mixing bassanite produced from waste gypsum boards with coal ash and blast-furnace slag, and revealed that ettringite formed in the material is extremely effective in immobilizing the fluorine derived from waste gypsum boards.

This composite recycled material is made by mixing the above-mentioned bassanite with coal ash as an alumina source and blast-furnace slag as a calcium oxide source so that the amount of ettringite produced is maximized chemically equivalent, suggesting that it is effective not only immobilizing fluorine but also immobilizing heavy metals such as hexavalent chromium and cadmium. As mentioned in Chapter 4 of this paper, the composite recycled material has hydraulic properties due to the base materials, bassanite derived from waste gypsum boards and Type II anhydrite gypsum, and therefore is effective as a soil improvement material.

In Section 1 of this chapter, we provide an overview of the Soil Contamination Countermeasures Act (hereinafter referred to as the Soil Contamination Countermeasures Act) and its soil environmental standards. In Section 2, we investigate the effectiveness of a composite recycled material based on bassanite derived from waste gypsum boards in immobilizing heavy metals, by using simulated wastewater containing dissolved heavy metals²⁷⁾. In Section 3, we investigate the applicability of the composite recycled material to actual contaminated soil contaminated with arsenic, lead, and the like, to verify its effectiveness as an immobilizer for heavy metals⁶⁴⁾.

5.1 Soil Contamination Countermeasures Act and Environmental Standards

5.1.1 Background of Soil Contamination Countermeasures Act

After the postwar reconstruction, our nation experienced affluence, convenience, and a sense of dreams and hopes through the mass production, mass consumption, and mass disposal of industrial products. However, this period of high economic growth came at a cost, leaving our nation with issues such as pollution, environmental destruction, and even global warming.

Air pollution, water pollution, noise, vibration, odor, land subsidence, and soil pollution, known as the seven typical forms of pollution, were addressed with various measures, while these measures resulted in side effects,

including health damage and environmental destruction. Among the measures, the Soil Contamination Countermeasures Act, which was the most delayed in its implementation, more than 10 years behind Europe and the US, was enacted in 2003. The laws on the other six pollutions (air pollution, water pollution, noise, vibration, odor and land subsidence) had been in force for a quarter of a century already. They aim to prevent the occurrence of pollution and the spread of damage by regulating the discharge concentration and discharge amount of by-products and wastes from industrial activities. In contrast to these laws, the Soil Contamination Countermeasures Act aims to grasp the status of soil that has been contaminated in the past and to take measures to prevent health damage to humans caused by ingestion of groundwater or direct ingestion of contaminated soil. This is why it is named the Soil Contamination Countermeasures Act rather than the Soil Contamination Prevention Act.

Under this Act, landowners are required to conduct soil surveys when modifying land that meets certain requirements. Soil surveys first look back at the land's history from the land registry and the like. If the survey confirms that a factory or other business existed there before, the following are investigated: what was manufactured, and what were the raw materials, the presence/absence of any related chemicals, fuel, and/or cleaning oil used in the process. If the literature survey suggests the possibility of soil contamination, a boring survey is conducted as a general survey to investigate whether the soil and groundwater are contaminated. If soil contamination exceeding environmental standards is discovered, the landowner is obligated to conduct a detailed survey to clarify the contaminant, the scope of contamination, and the concentration of contamination, report it to the government, and take measures.

Specific countermeasures include taking measures to prevent contamination from spreading through groundwater, as well as deciding on a soil purification policy according to the purpose of land use and implementing the measures. As for contamination by heavy metals which are the second-class specified hazardous substances, it is critical for us to consider both aspects of the leaching amount standard (mg/L) and the content standard (mg/kg) of contaminated soil. Generally, immobilizing treatment is the most common countermeasure, but if the content standard of the contaminant exceeds the environmental standard,

measures such as excavating and removing the contaminated soil itself or washing and purifying it are required.

5.1.2 Environmental Standards for Soil

The Soil Contamination Countermeasures Act specifies 26 types of specific hazardous substances as national environmental standards for soil. These include 11 types of volatile organic compounds (VOCs) as type 1 specific hazardous substances, 10 types of heavy metals as type 2 specific hazardous substances, and 5 types of pesticides as type 3 specific hazardous substances, totaling 26 types. The regulatory standards include those for the leaching amount into water and the amount of content.

Specifically, the type 2 specific hazardous substances that are the subject of study in this section include heavy metals such as mercury (Hg), cadmium (Cd), lead (Pb), and hexavalent chromium (Cr(VI)). Their effects on the body are known as pollution diseases, such as Minamata disease caused by mercury, and Itai-itai disease caused by cadmium. Minamata disease is a central nervous system disease caused by poisoning with methylmercury, with symptoms including ataxia, sensory impairment, and hearing impairment. The main symptoms of Itai-itai disease are multiple proximal renal tubule dysfunction and osteomalacia.

These heavy metals are thought to exist in the soil in the form of compounds such as oxides, hydroxides, and sulfides. It is known that heavy metals are strongly influenced by the hydrogen ion concentration in the presence of groundwater and are eluted, existing in the ionic state of atomic carriers. As such, heavy metals are harmful even in the form of atoms or ions alone and therefore cannot be decomposed and rendered harmless like the first and third-class specified hazardous substances. Accordingly, when using their physical properties to remove heavy metals from soil, the challenge is that many of them have relatively high melting and boiling points, which consume a large amount of energy and increase purification costs.

As mentioned above and in the previous section, it is effective to focus on the fact that many heavy metal compounds are attached to the surface of soil particles and to apply a washing method for classifying the small grain size of contaminated soil, such as silt and clay, to reduce the heavy metal content in the soil. In addition, when the content meets the standard but the leaching amount exceeds the standard, it is often economically

advantageous to apply an immobilizer and the like.

5.2 Immobilization of Fluorine, Hexavalent Chromium, Cadmium, and Lead, Using a Composite Recycled Material

Recycled gypsum produced by removing paper and foreign matter from waste gypsum board contains fluorine. To use it as a soil improvement material, attention must be paid to the leaching of fluorine, as mentioned in Chapter 3 of this paper.

A previous study²⁸⁾ conducted by the author and colleagues used industrially-adjusted kaolin with a high water content (140%) resembling soft ground, to which bassanite produced from recycled gypsum was added together with blast-furnace slag cement type B, and examined the relationship between the amount of cement added and the eluted fluorine concentration (mg/L). The study reports that, in the case of test specimens to which no blast-furnace slag cement type B was added, the fluoride leaching concentration exceeded the soil environmental standard of 0.8 mg/L with just 10% bassanite addition, whereas in the case of test specimens where 5% blast-furnace slag cement type B was added to the same kaolin, the fluoride leaching concentration was significantly below the soil environmental standard, even with 50% bassanite addition.

Furthermore, based on a previous research report²⁹⁾ describing that ettringite is effective in immobilizing fluorine, the relationship between the amount of ettringite produced in the test specimen and the eluted fluorine concentration was examined. Here, ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) is a hydrate of gypsum (CaSO₄), alumina (Al₂O₃), calcium oxide (CaO) and water (H₂O), and is generally known to be produced by a pozzolanic reaction in an alkaline environment³⁰⁾. These facts point out that the amount of ettringite produced in the test specimen (which is evaluated by X-ray diffraction intensity) is likely to control the alumina content of kaolin.

In addition, in a previous study conducted by the author and colleagues³¹⁾, we prepared specimens using only bassanite as the base material, with no kaolin to prevent minerals such as alumina (Al₂O₃) and calcium oxide (CaO) contained in kaolin from acting as a disturbing factor in the formation of ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O), and investigated the relationship between the amount of ettringite formed and the eluted

fluorine concentration by changing the amount of blast-furnace slag cement type B added. We reported in the study that, as a result, with various amounts of blast-furnace slag cement type B added to the base bassanite, the alumina and calcium oxide contained in blast-furnace slag cement type B formed ettringite through a pozzolanic reaction with the bassanite, and the amount of ettringite formed was extremely closely correlated with the amount of blast-furnace slag cement type B added, thereby revealing that there was a close correlation with the eluted fluorine concentration.

We concluded that increasing the amount of ettringite formed in bassanite is the most effective way to immobilize fluoride. We also presumed that the amount of ettringite formed is controlled by the alumina content in blast-furnace slag cement type B. Moreover, since this means that the alumina in the test specimens decreases to an insufficient chemical equivalent, we asserted that adding coal ash or other supplementary additives as an alumina source is economically significant.

Based on the above study results, we noticed that increasing the amount of ettringite produced is extremely effective in immobilizing fluorine. Hence, we devised a composite recycled material that is based on bassanite produced from waste gypsum board and is mixed with industrial by-products coal ash and blast-furnace slag. This composite recycled material was made by adding coal ash as an alumina (Al₂O₃) source and blast-furnace slag as a calcium oxide (CaO) source to the base material bassanite (CaSO₄·1/2H₂O) and determining the mixture that produces the maximum amount of ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) chemically equivalent.

Next, we increased the amount of blast-furnace slag cement type B added as an alkaline stimulant to this composite recycled material, and investigated the relationship between the amount of ettringite produced (evaluated by X-ray diffraction intensity) and the eluted concentration of fluorine derived from the recycled gypsum. As a result, when 0-4% of the alkaline stimulant was added to the composite recycled material, the amount of ettringite formed increased sharply, with the added amount of 4-32%, the amount of ettringite formed only increased only slightly³²⁻³⁴⁾.

The composite recycled material produced from these industrial by-products that are the subject of our research functions as a soil improvement material and a soil solidification material for mud and soft ground. The

composite recycled material can be extremely effective if having the ability to immobilize heavy metals.

In this section, we investigate the effectiveness of the composite recycled material, which is based on bassanite derived from waste gypsum, for the immobilization of heavy metals. Specifically, we focus on hexavalent chromium (Cr(VI)), cadmium (Cd), and lead (Pb), which are frequently reported in soil heavy-metal contamination cases³⁵⁻³⁹⁾. We prepared simulated heavy-metal contaminated water with adjusted concentrations and directly added and mixed the simulated contaminated water with this composite recycled material to create test specimens. We then investigated the relationship between the curing time and the leaching concentration of these heavy metals, verifying the geoenvironmental effectiveness of the composite recycled material.

5.2.1 Materials Used in Experiment and Reagents for Simulated Contaminated Water

(1) Bassanite

The characteristics of bassanite are described in detail in Chapter 3 of this paper, and we will not discuss them here.

(2) Coal ash

Coal ash is produced as a by-product in coal-fired thermal power plants. When inorganic components (ash) contained in coal melt during coal combustion, they fly out of the boiler in a ball shape and are captured by an electrostatic precipitator or the like. We call the captured substance “fly ash.”

The substance that does not fly out of the boiler but melts and accumulates at the bottom of the boiler is cooled and crushed. We call the crushed material "clinker ash," which is comprised of the same components as those of fly ash. Both are effectively used as civil engineering materials, such as cement raw materials and artificial aggregates.

In recent years, after all nuclear power plants were shut down due to the Great East Japan Earthquake, coal-fired thermal power plants have been restarted, and new construction of such plants has progressed, which has increased coal consumption. As a result, the annual generation of fly ash and clinker ash has increased from 10 million tons before the earthquake to nearly 13 million tons.

Table 4: Main chemical components of coal ash used in the study in this section (%)²⁷⁾

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
58.3	27.6	4.2	2.8	1.1

Table 5: Main chemical components of blast-furnace slag used in the study in this section²⁷⁾

Component	Ratio (%)
SiO ₂	33.6
Al ₂ O ₃	14.3
Fe ₂ O ₃	0.2
CaO	42.5
MgO	7.3
SO ₃	0.9
TiO	1.2
MnO	0.2

Table 6: Main chemical components of blast-furnace cement Type B used in the study in this section²⁷⁾

Component	Ratio (%)
SiO ₂	26.3
Al ₂ O ₃	8.7
Fe ₂ O ₃	1.9
CaO	54.1
MgO	3.7
SO ₃	2.0

In the study presented in this section, we used JIS II standard fly ash (JIS A 6201). This ash is commercially available as a civil engineering material, and has a density of 1.95 g/cm³ or more and a fineness (Blaine method) of 2,500 or more. The main chemical components of coal ash are shown in **Table 4**²⁷⁾. As shown in the table, silica (SiO₂) accounts for the majority at 58.3%, alumina (Al₂O₃), which is a component of ettringite, is included at 27.6%, and calcium oxide (CaO) at 2.8%. Therefore, coal ash seems effective as a supplementary additive for alumina sources.

However, it is important to note that since fly ash has experienced high temperatures through the combustion of coal, the particle surface has been melted and vitrified (amorphized). Therefore, the pozzolanic reaction does not proceed unless the fly ash is placed in an alkaline environment.

(3) Blast-furnace slag

A blast furnace is a vertical furnace for producing iron by mixing iron ore and coke, heating them to high temperatures, and reducing the iron oxide, the main

component of iron ore, with the coke. To increase the purity of the iron, quicklime (CaO) is added to the blast furnace, and the quicklime absorbs and separates the impurities contained in the iron ore. Blast-furnace slag is produced by rapidly cooling the quicklime that has melted and absorbed the impurities. Around 24 million tons of blast-furnace slag are generated annually, and are effectively used as a cement raw material, roadbed material, and others.

In the study presented in this section, blast-furnace slag powder (JIS A 6402) was used which is commonly available as a civil engineering material with a density of 2.89 g/cm³ and a fineness (Blaine method) of 4,700. The major chemical components of blast-furnace slag are shown in **Table 5**²⁷⁾. As shown in the table, it contains 33.6% silica (SiO₂), 14.3% alumina (Al₂O₃), which would be a component of ettringite, and 42.5% calcium oxide (CaO). This suggests that blast-furnace slag is extremely effective as a supplementary additive for calcium oxide and alumina sources.

However, it is important to note that since blast-furnace slag has experienced high temperatures, it has been melted and vitrified (amorphized), similar to the coal ash. Therefore, the pozzolanic reaction does not proceed unless the blast-furnace slag is placed in an alkaline environment.

(4) Blast-furnace slag cement type B

Blast-furnace slag cement is produced by mixing blast-furnace slag with cement clinker, and its quality is regulated by Japanese Industrial Standard (JIS) R 5211. Depending on the mixing ratio of blast-furnace slag, it is regulated as type A (more than 5% and less than 30%), type B (more than 30% and less than 60%), and type C (more than 60% and less than 70%).

In the study presented in this section, we used blast-furnace slag cement type B, which is generally available commercially as a civil engineering material with a density of 3.04 g/cm³ and a fineness (Blaine method) of 3,750. The main chemical components of blast-furnace slag cement type B are shown in **Table 6**²⁷⁾. As shown in the table, it contains 8.7% alumina, which is a component of ettringite, and 54.1% calcium oxide. An excessive amount of cement added as a cement stabilizing material raises a concern about the leaching of hexavalent chromium. Therefore, it is desirable to keep the cement addition rate as low as possible.

In the study presented in this section, blast-furnace slag

cement type B was used as an alkaline stimulant to induce the pozzolanic reaction.

(5) Hexavalent chromium (Cr(VI))

Hexavalent chromium, known for its strong oxidizing properties, reacts with organic matter to form the more stable trivalent chromium. However, hexavalent chromium is extremely toxic. Due to its toxicity, environmental standards for soil strictly limit its leaching amount to 0.05 mg/L or less. Even if under the limited amount, when dissolved in rainwater, hexavalent chromium can mix with groundwater, posing a threat to drinking water. In nature, chromium typically exists as trivalent chromium, but it can be converted to hexavalent chromium through oxidation in high-temperature environments. Cement, in particular, is believed to contain hexavalent chromium due to its manufacturing process.

In the study presented in this section, potassium dichromate (K₂Cr₂O₇), which has a relatively high solubility in water among chromium compounds, was used as a reagent. Potassium dichromate is a red-orange crystal with a density of 2.67 g/cm³, a melting point of 398°C, a boiling point of 500°C, and a solubility in water of 149 g/L (0°C).

(6) Cadmium (Cd)

Cadmium has been widely used in alloys of copper, silver, nickel, and other metals, as well as in storage battery electrodes. During the manufacturing, intermediate treatment, and final disposal processes, cadmium can disperse into the atmosphere or mix with wastewater. Cadmium is harmful to human health, with the most well-known example of environmental damage being the Itai-itai disease in Japan. Therefore, environmental standards for soil strictly limit cadmium leaching to 0.01 mg/L or less. Like hexavalent chromium, cadmium is a pollutant and can dissolve in rainwater, mix with groundwater, and threaten drinking water supplies.

In the study presented in this section, the reagent was cadmium chloride (CdCl₂) which has a relatively high solubility in water among cadmium compounds. Cadmium chloride is a colorless solid, and is white in powder form. It has a density of 4.047 g/cm³, a melting point of 568°C, a boiling point of 964°C, and a solubility in water of 90 g/L (0°C).

(7) Lead (Pb)

Lead has been commonly used in glass and battery electrodes as their compound and in gunpowder as its raw material. It has also been used since ancient times in red pigments such as Komyotan. Lead is a heavy metal such familiar to humans. Lead poisoning is cumulative in the human body, leading to symptoms that include loss of appetite, anemia, and decreased urination. Due to these health concerns, the environmental standards for soil have established strict leaching limits at 0.01 mg/L or less.

In the study presented in this section, lead nitrate (II) (Pb(NO₃)₂) was used, as a reagent, which has a relatively high solubility in water among lead compounds. Lead nitrate (II) is a colorless solid and is white in powder form. Lead nitrate (II) has a density of 4.53 g/cm³, a melting point of 470°C, and a boiling point that does not exist because it decomposes at the melting point of 470°C. Its solubility in water is 52 g/L (20°C).

5.2.2 Experimental Method

(1) Preparation of Composite Recycled Material and Simulated Contaminated Water

A composite recycled material was prepared based on a mix design that maximizes the amount of ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) produced chemically equivalent from the composition ratios of alumina (Al₂O₃), calcium oxide (CaO), and bassanite (CaSO₄·1/2H₂O) contained in coal ash, blast-furnace slag, and bassanite . With the material, a hydration reaction of 3 mol of calcium oxide and 3 mol of gypsum with 1 mol of alumina produces 1 mol of ettringite⁴⁰⁻⁴⁹⁾.

As mentioned above, compounds of heavy metals that are highly soluble in water were selected as reagents for the simulated contaminated water. Therefore, a leaching test was conducted under more severe conditions for the composite recycled material as an immobilizer for heavy metals.

The concentration factor of the simulated contaminated water to be added was gradually increased, and the concentration factor at which the leaching concentration from the test specimen exceeds the environmental standard was identified in advance, and then the relationship between the curing time and the leaching concentration was examined.

(2) Preparation of Specimens, The Curing, and Preparation of Test Solutions

In the study presented in this section, to figure out the relationship between the amount of ettringite produced and the leaching concentration of heavy metals with respect to the curing time, the mixing for specimens was designed to be provided by the composite recycled material as the base material, without using soil which is considered to be a disturbance factor for ettringite production. For the preparation of a specimen, 4% blast-furnace slag cement type B was added to the composite recycled material as an alkaline stimulant for each heavy metal. Another specimen was prepared without adding blast-furnace slag cement type B as a blank test. The blank test was carried out to clarify the difference in the immobilization (adsorption) performance of ettringite produced in the composite recycled material against heavy metals and the immobilization (adsorption) performance of materials (gypsum, blast-furnace slag, and coal ash) other than ettringite. In addition, the simulated contaminated water portion of each concentration was added to the composite recycled material so that the water content reached 100%, followed by stirring. The six curing times for each specimen were determined to be 1, 3, 5, 168, 336, and 504 hours, and the specimens were cured in the air for the specified curing times in an environment of room temperature (20 ± 2°C) and relative humidity (35-45%).

For the specimens after the specified curing times, test solutions were prepared for hexavalent-chromium leaching tests, cadmium leaching tests, and lead leaching tests.

5.2.3 Relationship between Amount of Ettringite Formed in Composite Recycled Material and Leaching Concentration of Fluorine

Figure 7³³⁾ shows the relationship between the amount of ettringite formed (measured by X-ray diffraction intensity) in composite recycled materials after a 4-week curing period, which was revealed in a previous study³³⁾ by the author and colleagues, and the leaching concentration of fluorine. The bassanite, which is the base material of the composite recycled material, is derived from waste gypsum board, and thereby the leaching concentration of fluorine may exceed the environmental standard for soil. However, The figure indicates that the ettringite formed by the pozzolanic reaction in the composite recycled material decreased the fluorine leached.

The figure shows that the amount of ettringite increased sharply when a C/M ratio (%) (where C is

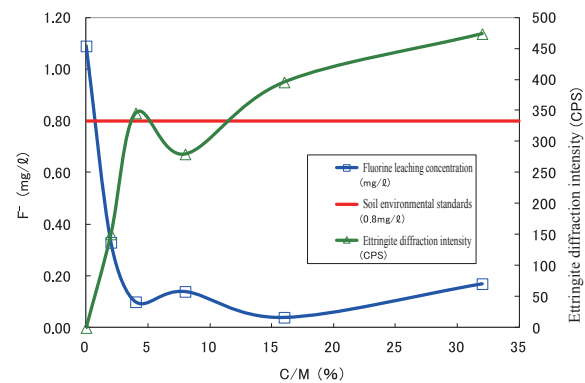


Figure 7: Relationship between C/M ratios and fluorine leaching concentration/X-ray diffraction intensity of ettringite (CPS)³³⁾

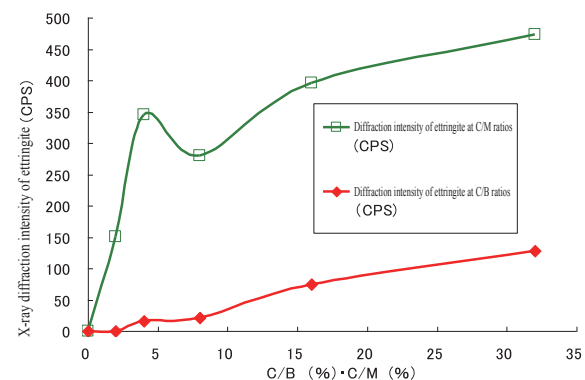


Figure 8: Relationship between C/B and C/M ratios and X-ray diffraction intensity of ettringite (CPS)³³⁾

blast-furnace slag cement type B, and M is composite recycled material) is in the range of 0 to 4%, and the eluted fluorine concentration decreased sharply in tandem with this increase. Furthermore, when the C/M ratio (%) was in the range of 4 to 32%, the amount of ettringite formed increased gradually, with the eluted fluorine concentration remaining in the range of 0.1 to 0.2 mg/L, which is significantly lower than the environmental standard for soil of 0.80 mg/L. No further decrease in the eluted fluorine concentration was observed in this range.

Next, **Figure 8³³⁾** shows a comparison of the relationship between a C/B ratio (%) (where B is bassanite) and the amount of ettringite formed when blast-furnace slag cement type B was added to bassanite produced from recycled gypsum, to the relationship between a C/M ratio (%) and the amount of ettringite formed when blast-furnace slag cement type B was added to the composite recycled material. It is clear from the figure that the amount of ettringite formed from the composite recycled material was 5 to 10 times greater than that from bassanite.

When focusing on the case with the bassanite produced from recycled gypsum, the amount of ettringite formed

was controlled by C/B ratios (%) because the alumina and calcium oxide required for ettringite formation are limitedly supplied from the blast-furnace slag cement type B only. As a result, the amount of ettringite increased almost proportionally with an increase in C/B ratios (%). In contrast, in the case with the composite recycled material, the mix was designed to maximize the amount of ettringite formed. Therefore, we believe that a pozzolanic reaction by the alkaline stimulant (i.e., the blast-furnace slag cement type B) progressed for the C/M ratio (%) in the range of 0.0 to 4.0%, causing the amount of ettringite generated to increase rapidly.

In the study presented in this section, blast-furnace slag cement type B was selected as an alkaline stimulant due to its reasonable cost and commercial availability. It is a well-known fact that cement is effective in immobilizing heavy metals. To minimize the influence of cement in the study, as can be seen from the figure, the amount of cement added was limited to a C/M ratio of 4.0%. At this ratio, the amount of ettringite produced by the pozzolanic reaction accounts for more than 70% of the total amount produced, and the ratio was considered to be necessary and sufficient for immobilizing heavy metals.

It should be noted that powder X-ray diffraction was applied as a method for quantifying the ettringite in the study in this section. However, there are new methods using solid-state ²⁷Al NMR and previous research reports that have revealed the effects of drying and separation for powder X-ray diffraction⁵⁰⁻⁵¹⁾. Furthermore, similar to the study in this section, there are known research reports⁵²⁻⁵³⁾ on soil solidifying technology and suppression of leaching of heavy metal by using industrial by-products.

In the following, we examine the effectiveness of the composite recycled material in immobilizing heavy metals such as hexavalent chromium (Cr(VI)), cadmium (Cd), and lead (Pb).

5.2.4. Immobilization of Hexavalent Chromium (Cr(VI))

Figure 9²⁷⁾ shows the relationship between the leaching concentration of hexavalent chromium and the curing time for test specimens. These specimens were prepared by adding simulated contaminated water that contained hexavalent chromium adjusted to a concentration 1,000 times the soil environmental standard, to achieve 100% water content. The soil environmental standard allows for hexavalent chromium

to be eluted up to 0.05 mg/L. In this study, the leaching concentration was examined using specimens that contained hexavalent chromium at 10, 100, 1,000, and 10,000 times the standard. The figure shows the multiples of the ranges where the leaching concentration approached the same standard. For the specimens with 10 and 100 times concentrations, the values satisfied the soil environmental standard of 0.05 mg/L and fell below the lower limit of analysis. Accordingly, the figure shows the results of the addition of contaminated water adjusted to a concentration of hexavalent chromium ions in potassium dichromate (K₂Cr₂O₇) at 1,000 times the environmental standard. The calculated hexavalent chromium content in this case was 50 mg/kg. Along with this test, a specimen was prepared without adding an alkaline stimulant to the composite recycled material, and a leaching test was conducted as a blank test.

Since the figure is a log-log plot, it appears that there was little change. When we look at the blank test specimens, there is no significant change in the leaching concentration (2.22-2.29 mg/L) from 0 to 168 hours (1 week) either. This suggests that hexavalent chromium is adsorbed onto the minerals contained in the composite recycled material even without the formation of ettringite. Then, a gradual decrease in the leaching concentration (2.29 to 1.33 mg/L) was observed from 168 hours (1 week) to 504 hours (3 weeks). This suggests that, in a small amount, compounds such as monosulfate (3CaO·Al₂O₃·CaSO₄·12H₂O) and calcium aluminoferrite (6CaO·2Al₂O₃·Fe₂O₃), which are precursors of ettringite, were formed in the composite recycled material as the curing time increased, leading to absorption of hexavalent chromium⁵⁵⁻⁵⁷⁾.

Next, looking at the specimens to which the alkaline stimulant was added, no significant change in the leaching concentration (2.20-1.78 mg/L) was observed during the curing period from 0 to 5 hours, as with the blank test specimens. However, the leaching concentration decreased (1.85 to 0.41 mg/L) from 5 to 168 hours of curing. Furthermore, the leaching concentration (0.41 to 0.12 mg/L) decreased over the course of 2 to 3 weeks of curing. Eventually, it did not reach the soil environmental standard of 0.05 mg/L. However, it was predicted to converge to about 0.10 mg/L, which is twice the concentration. Since previous studies⁵⁸⁻⁶⁰⁾ have reported that ettringite is effective in immobilizing hexavalent chromium, it is presumed that the difference in the leaching concentration of hexavalent chromium occurred

due to the difference in the amount of ettringite produced during the curing period.

On the other hand, previous research⁶³⁾ has shown that the pH of soil has a large effect on the leaching concentration of heavy metals. Below, we consider the effect of the pH of the test specimens in the study in this section.

First, when only distilled water was added to the composite recycled material to achieve 100% water content, the pH value was 6.8 to 7.3. This is likely because coal ash and blast-furnace slag, which are the raw materials of the composite recycled material, are inferred to have undergone vitrification, making them insoluble in water due to the thermal history during their formation process. As a result, little hydroxide (alkaline) was produced when reacting with water (distilled water).

Next, simulated contaminated water with a concentration of 1,000 times that of potassium dichromate (K₂Cr₂O₇) dissolved in distilled water was added to the composite recycled material to prepare specimens. The pH value of the blank test specimen without the addition of an alkaline stimulant was 5.0 to 5.2, which is weakly acidic, and the pH value of the specimen with the addition of an alkaline stimulant was 11.2 to 11.6, which is alkaline. In this case, it is presumed that the addition of 4.0% blast-furnace slag cement type B as an alkaline stimulant created an alkaline environment for the composite recycled material, dissolving the vitrified coal ash and blast-furnace slag, and generating hydroxide and ettringite in a chain reaction.

According to a study by Kida et al.⁶³⁾ on the leaching concentration of heavy metals from incineration ash of municipal waste, the leaching concentration of chromium, which is an amphoteric metal, is lowest at a pH value of around 7, and the leaching concentration increases when the pH value both decreases (becomes acidic) and increases (becomes alkaline) from this point.

Based on the above findings and assuming the results of the study by Kida et al.⁶³⁾, there is a contradictory relationship between the increase in the leaching concentration of chromium in an alkaline environment with a pH value of 7 or more of the test specimen and the decrease in the leaching concentration of chromium due to the increase in the amount of ettringite formed.

Therefore, the study in this section suggests that, between 168 and 504 hours when the amount of delayed-acting ettringite formed is likely to increase, ettringite overcomes the effects of the alkali, causing a

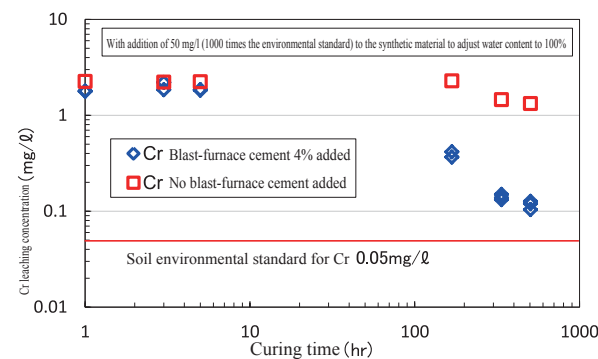


Figure 9: Relationship between curing time (hr) and Cr leaching concentration (mg/L)²⁷⁾

significant decrease in the leaching concentration of chromium.

5.2.5 Immobilization of Cadmium (Cd)

Figure 10²⁷⁾ shows the relationship between the cadmium leaching concentration and curing time for the test specimens. The specimens were prepared by adding simulated cadmium-contaminated water (adjusted to a concentration 10,000 times the soil environmental standard) to achieve 100% water content. The soil environmental standard for cadmium allows 0.01 mg/L as the leaching amount. As in the case of hexavalent chromium, when the relationship between the leaching concentration and curing time was examined at each concentration magnification, a significant change was observed in the range of 10,000 times the concentration as shown in the figure. The cadmium content at this time was 100 mg/kg. In addition, as in the case of hexavalent chromium, a test specimen was prepared without adding an alkaline stimulant to the composite recycled material, and a leaching test was conducted as a blank test. First, focusing on the blank test specimen, no change in the leaching concentration (0.65-0.60 mg/L) was observed from 0 to 5 hours of curing, and the leaching concentration decreased (0.03 to 0.001 mg/L) between 5 and 168 hours (1 week). Furthermore, from 336 to 504 hours (2 to 3 weeks), it decreased to a value below the environmental standard for soil (0.001 mg/L). We presume that minerals other than ettringite, which are effective in immobilizing cadmium, were formed without any addition of alkaline stimulant, as in the case of hexavalent chromium. Since cadmium chloride (CdCl_2) was used as the cadmium-contaminated water, it is possible that chloride ions and components of the composite recycled material combined to form new minerals.

Next, focusing on the specimen to which an alkaline stimulant was added, the figure shows that the concentration remained consistently at 0.001 mg/L, which is 1/10 of the environmental standard. This indicates that the composite recycled material is extremely effective in immobilizing cadmium under the conditions of the study in this section. However, this case suggests that the immobilization of cadmium in an alkaline environment and the adsorption performance of ettringite work synergistically.

Hereinafter, as in the case of hexavalent chromium, we consider the effect of the pH of the test specimens used in the study in this section.

First, the pH value of the simulated contaminated water with cadmium chloride dissolved in it at a concentration of 10,000 times that of the standard was 6.8. Next, when this simulated contaminated water was added to the composite recycled material and a test specimen was prepared, the pH value of the blank test specimen without cement was almost neutral at 6.2 to 6.9, and the test specimen with an alkaline stimulant added was alkaline at 11.4 to 11.9. In the case where 4.0% blast-furnace slag cement type B was added as an alkaline stimulant, it is presumed that the pozzolanic reaction was progressing rapidly for the same reason as in the case of hexavalent chromium.

Cadmium forms hydroxides such as cadmium hydroxide ($\text{Cd}(\text{OH})_2$) with low solubility in an alkaline environment. Therefore, it is presumed that the cadmium leaching concentration in the test specimen with a pH value of 11.4 to 11.9, to which an alkaline stimulant was added, was consistently below 0.001 mg/L due to the influence of alkali. In the blank test with a neutral pH value of 6.2 to 6.9, no change in the leaching concentration was observed from 0 to 5 hours of curing time, as it was not affected by either alkali or ettringite. In

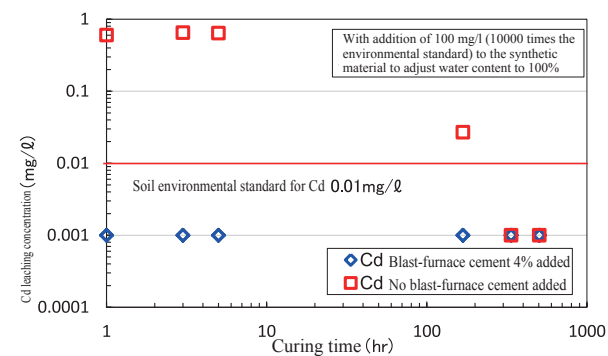


Figure 10: Relationship between curing time (hr) and Cd leaching concentration (mg/L)²⁷⁾

the 336 to 504-hours period, as mentioned above, it is suggested that minerals other than ettringite, which are effective in immobilizing cadmium, were formed.

5.2.6 Immobilization of Lead (Pb)

Figure 11²⁷⁾ shows the relationship between the lead leaching concentration and curing time for test specimens. The specimens were prepared by adding simulated lead-contaminated water (adjusted to a concentration 10,000 times the soil environmental standard) to achieve 100% water content. The soil environmental standard for lead allows 0.01 mg/L as the leaching amount, and as in the case of cadmium, when the relationship between the leaching concentration and curing time at each concentration magnification was examined, a significant change was observed in the range of 10,000 times the concentration shown in the figure. The lead content at this time was 100 mg/kg. Along with this test, as in the case of hexavalent chromium, a test specimen was prepared without adding an alkaline stimulant to the composite recycled material, and a leaching test was conducted as a blank test.

The figure shows that the lead leaching concentration decreased (from 0.02 to 0.001 mg/L) over the entire range of curing time, regardless of whether an alkaline stimulant was added or not. This suggests that lead nitrate ($\text{Pb}(\text{NO}_3)_2$) in the lead-contaminated water may have combined with the components of the composite recycled material to produce a new mineral. Previous studies have reported that ettringite is effective in immobilizing lead^{61~62)}.

Hereinafter, as with the cases of hexavalent chromium and cadmium, we consider the effect of the pH of the specimens used in this study.

First, the pH value of the simulated contaminated water with lead nitrate dissolved in it at a concentration of 10,000 times that of the standard was 3.5, which is acidic. Next, when this simulated contaminated water was added to the composite recycled material to create specimens, the pH value of the blank test specimen without cement was acidic at 3.8 to 4.2, while the pH value of the specimen with the addition of an alkaline stimulant was alkaline at 10.8 to 11.2. In this case, it is presumed that the pozzolanic reaction was progressing rapidly due to the action of the alkaline stimulant.

In addition, according to a study by Kida et al.⁶³⁾ which investigated the leaching concentration of heavy metals from incineration ash of general waste, the leaching

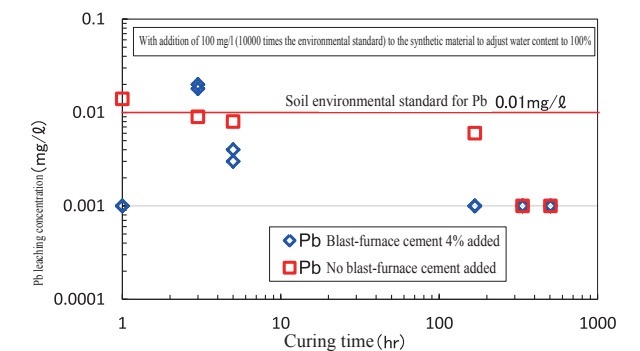


Figure 11: Relationship between curing time (hr) and Pb leaching concentration (mg/L)²⁷⁾

concentration of lead, which is an amphoteric metal, is lowest at a pH value of around 9, and the leaching concentration increases whether the pH is lowered (acidic) or increased (alkaline) from this point.

Based on these findings and assuming the results of the research by Kida et al.⁶³⁾, there is a contradictory relationship between the increase in the eluted lead concentration in an alkaline environment with a pH value of 9 or higher of the test specimen and the decrease in the eluted lead concentration due to the increase in the amount of ettringite formed. Therefore, the study in this section suggests that between 168 and 504 hours when the amount of delayed-acting ettringite formed is likely to increase, ettringite overcomes the effects of the alkali, causing a significant decrease in the leaching concentration of lead.

5.3 Immobilization of Actual Contaminated Soil Using Composite Recycled Materials

In the previous section, we demonstrated that the composite recycled material based on bassanite derived from waste gypsum boards is extremely effective in immobilizing heavy metals, by using simulated contaminated water containing hexavalent chromium, cadmium, and lead. In this section, we apply this composite recycled material to actual contaminated soil that is multiplex-contaminated with arsenic, hexavalent chromium, lead, and the others⁶⁵⁻⁶⁸⁾ and examine its effectiveness as a more practical immobilizer.

5.3.1 Preparation of Actual Contaminated Soil Specimens and Test Solutions

The actual contaminated soil used as samples in this study⁶⁴⁾ was obtained from soil generated during tunnel construction. In the soil, the results of a preliminary leaching test showed that the leaching concentrations of

arsenic (As), as well as those of lead (Pb) and hexavalent chromium (Cr(VI)), exceeded the soil environmental standards. The actual contaminated soil samples were classified into three types, A, B, and C, based on the differences in the sampling locations. Sample A is mainly sandy soil with little clay and silt. Samples B and C are mainly clay and silt.

Next, based on the results of the preliminary leaching test, it was predicted that Sample A, which exhibited the lowest As-leaching concentration, would show a leaching concentration below the soil environmental standards within the M/S ratios (%) of 0 to 10% (where M is immobilizer, and S is actual contaminated soil), that is, a relatively small amount of immobilizer added. Therefore, to enhance accuracy within this range, the M/S ratios (%) were set to 0, 5, 10, and 20%. In contrast, for Samples B and C, which showed relatively high As-leaching concentrations, the range of immobilizer addition was expanded and the M/S (%) ratios were set to 0, 10, 20, and 40%. Here, the specimen with an M/S ratio of 0% was used in a blank test. For this blank test, all procedures from specimen preparation to curing and leaching tests were carried out in the same way as for the other specimens, and this was used as a benchmark to relatively examine the relationship between the M/S ratios (%) and leaching concentrations of heavy metals (mg/L).

In the study in the previous section²⁷⁾, since the subject was soft ground with a high water-content, distilled water was added to the dry sample and the immobilizer to achieve 100% water content, followed by stirring. Eventually a total of 36 specimens were prepared, three specimens for each predetermined M/S (%) value. These specimens were cured in air for four weeks in an environment of room temperature ($20 \pm 2^\circ\text{C}$) and relative humidity (35–45%).

To prepare the test solutions, the specimens that had passed the designated curing period were crushed in a mortar. Then, 100 g of water was added to 10 g of the crushed specimen, and the mixture was shaken in a stirrer for six hours. The supernatant was then filtered to prepare the leaching test solutions for arsenic, hexavalent chromium, cadmium, and lead. In this study⁶⁴⁾, factors such as impurities in the solvent, pH, and stirring time during leaching were considered to affect the leaching concentration of heavy metals. Additionally, to compare the results with the previous study on ettringite formation in the composite recycled material, the method for preparing the test solutions was based on the previous

studies by the author and colleagues^{27) 33) 34)}. Hence, distilled water was used as the solvent for preparing the specimens and for the dissolution test, as it is considered that differences in water quality have the least effect on the concentration of each heavy metal ion.

5.3.2 Immobilization of Arsenic (As) in Actual Contaminated Soil

Figure 12⁶⁴⁾ shows the relationship between the M/S ratio (%) and As-leaching concentration (mg/L). The soil environmental standard for arsenic allows leaching of 0.01 mg/L. First, looking at Sample A, the figure shows that at an M/S ratio of 0%, the As-leaching concentration was 0.014 to 0.028 mg/L (average value = 0.023 mg/L), which is 1.40 to 2.80 times the soil environmental standard, and at an M/S ratio of 5% or more, the As-leaching concentration was reduced to 0.005 to 0.001 mg/L, which is 1/2 to 1/10 of the soil environmental standard.

Next, looking at Sample B and C, at an M/S ratio of 0%, the As-leaching concentration was high, ranging from 3.616 to 3.884 mg/L (average value = 3.769 mg/L), which is 362 to 388 times the soil environmental quality standard. As the M/S ratio increased, the As-leaching concentration decreased in a gentle curve, falling far below 0.001 mg/L, which is 1/10 of the soil environmental quality standard, at an M/S ratio of 40%. The figure suggests that, in Samples B and C, the As-leaching concentration falls below the soil environmental quality standard of 0.01 mg/L at an M/S ratio of 30% or higher.

Regarding the difference in As-leaching concentration between Sample A and Sample B and C, we need to note that even though they were taken from the same tunnel construction site, Sample A was mainly sandy (2–0.075 mm) soil with little silt (0.075–0.005 mm) and clay (0.005 mm or less), whereas Sample B and C were mainly silt and clay. This fact demonstrates that Sample A has a smaller surface area per mass (specific surface area) than Sample B and C. Assuming that arsenic is uniformly attached to the soil particle surface, this likely explains the lower As-leaching concentration in Sample A. If we assume that the soil particles are spherical with uniform density without considering the shape and surface condition of the soil particles, the surface area per unit mass (specific surface area) will be n times larger when the average particle diameter is $1/n$ times smaller. Therefore, the average As-leaching concentration of Sample B and Sample C is $3.769/0.023 \approx 164$ times higher than the average As-leaching concentration of Sample A at an M/S ratio of

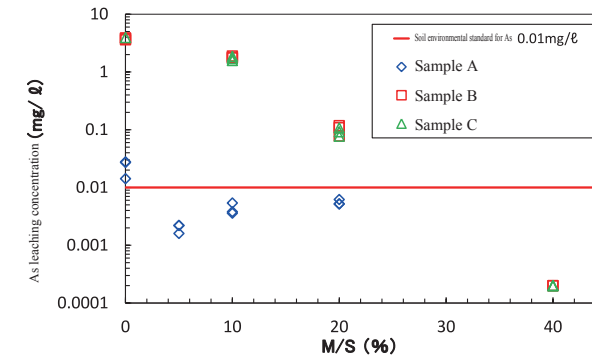


Figure 12: Relationship between M/S ratios (%) and As leaching concentration (mg/L)⁶⁴⁾

0%, leading to the estimation that the average particle size of Sample B and C is 1/64 times that of Sample A.

Arsenic in soil includes arsenic acid (H_3AsO_4) with As (V) and arsenous acid (H_3AsO_3) with As (III), and is adsorbed to iron and aluminum hydroxides as arsenate ions (H_2AsO_4^- , HAsO_3^{2-} , AsO_4^{3-}) in the presence of water. As the pH increases to 8.0–9.5 or higher, the amount of leaching arsenic tends to increase⁶⁹⁾. A high pH environment is required to generate ettringite. However, even under such conditions, the leaching concentration of arsenic in the experiment in this section started to decrease. This is likely because ettringite and other compounds synthesized from the composite recycled material contribute to the immobilization of arsenic.

The above description demonstrates that the composite recycled material used in this study in this section is effective as an immobilizer for arsenic-contaminated soil.

5.3.3 Immobilization of Hexavalent Chromium (Cr(VI)) in Actual Contaminated Soil

Figure 13⁶⁴⁾ shows the relationship between the M/S ratio (%) and Cr(VI)-leaching concentration (mg/L) when an immobilizer was applied to actual contaminated soil. The soil environmental standard for hexavalent chromium sets a leaching standard at 0.05 mg/L. The figure shows that at an M/S ratio of 0% for Sample A, the value ranged from 0.0003 to 0.0007 mg/L (average value = 0.0005 mg/L), which is equal to or less than 1/50 of the soil environmental standard. Even if the M/S ratio increases, it remains close to the lower analytical limit of the measuring instrument. As for the values for Samples B and C, at an M/S ratio of 0%, the values ranged from 0.076 to 0.038 mg/L (average value = 0.058 mg/L), which is 1.52 to 0.76 times the soil environmental standard. There is no significant change up to an M/S ratio of 20%, with values fluctuating between 0.03 and 0.02 mg/L, which is 1/1.7 to 1/2.5 times the soil environmental standard. At an

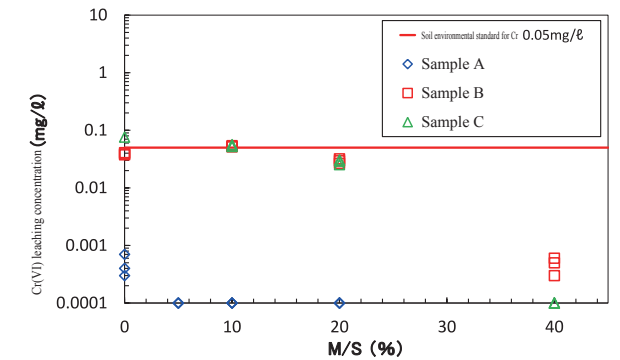


Figure 13: Relationship between M/S ratios (%) and Cr(VI) leaching concentration (mg/L)⁶⁴⁾

M/S ratio of 40%, the values were 0.001 mg/L or less, which is 1/50 of the soil environmental standard.

These results clearly show that the composite recycled material used in this study is effective as an immobilizer for actual soil that is contaminated with hexavalent chromium. The main factor of this effectiveness is thought to be the ettringite synthesized in the composite recycled material and its precursors such as monosulfate and calcium aluminoferrite⁵⁴⁾.

A previous study⁵⁸⁾ has also reported that ettringite is effective in immobilizing hexavalent chromium.

5.3.4 Immobilization of Lead (Pb) in Actual Contaminated Soil

Figure 14⁶⁴⁾ shows the relationship between the M/S ratio (%) and Pb-leaching concentration (mg/L) when an immobilizer was applied to actual contaminated soil. The soil environmental standard for lead sets a leaching standard at 0.01 mg/L. Focusing on the value of Sample A in the figure, at an M/S ratio of 0%, the value was 0.001 to 0.003 mg/L (average value = 0.002 mg/L), which is 1/10 to 1/3.3 times the soil environmental standard, and it fell below 0.001 mg/L as the M/S ratio increased. As for Sample B, at an M/S ratio of 0%, the value was 0.152 to 0.154 mg/L (average value = 0.153 mg/L), which is 15 times the environmental standard. At an M/S ratio of 10% or more, it decreased significantly, with values fluctuating between 0.003 and 0.005 mg/L, which is 1/3.3 to 1/2.0 times the soil environmental standard. At an M/S ratio of 0%, Sample C showed a value ranging from 0.674 to 0.688 mg/L (average value = 0.681 mg/L), which is 67 to 69 times the soil environmental standard. Like Sample B, it decreased significantly at an M/S ratio of 10% or more, showing leaching of 0.005 to 0.001 mg/L, which is 1/2 to 1/10 times the soil environmental standard.

These results clearly show that the composite recycled material used in the study presented in this section is

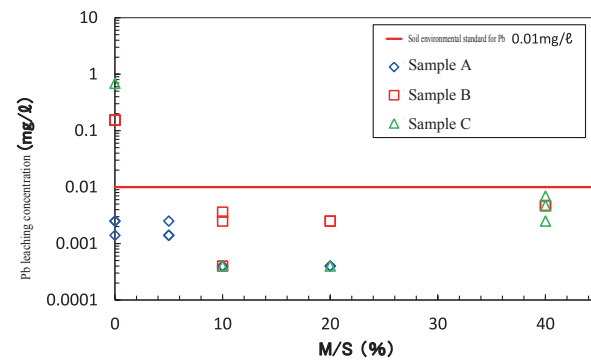


Figure 14: Relationship between M/S ratios (%) and Pb leaching concentration (mg/L) ⁶⁴⁾

effective as an immobilizer for actual soil that is contaminated with lead. The main factor is thought to be the ettringite synthesized in the composite recycled material and its precursor such as monosulfate. A previous study⁶¹⁾ has also reported that ettringite is effective in immobilizing lead.

5.3.5 Colors of Test Solutions from Actual Contaminated Soil

All test solutions (12 solutions) made from specimens of Sample A with M/S ratios of 0, 5, 10, and 20% were colorless and transparent, with no coloration or suspension observed. This is related to the fact that Sample A was mainly sandy soil with little silt and clay, and the leaching concentrations of heavy metals arsenic, hexavalent chromium, and lead were extremely small. In other words, this suggests that the specific surface area per unit mass of the soil particles was smaller than those of the other Samples. Consequently, the amount of heavy metals and other impurities, which contribute to the coloration of the test solutions, attached to the soil particle surface was reduced.

Next, the color changes of the test solutions generated from the specimens of Sample B and Sample C are shown in **Photos 2**⁶⁴⁾ and **3**⁶⁴⁾. In both photos, Part (a) shows the yellowish-brown solutions at an M/S ratio of 10%. No Tyndall phenomenon, in which the light path appears to be uniformly lit when light is irradiated from the side, occurred, verifying that no suspension was observed. Similarly, Part (b) shows light yellowish-brown solutions at an M/S ratio of 20%, and like Part (a), no suspension was observed. Similarly, Part (c) shows colorless and transparent solutions at an M/S ratio of 40%. It should be noted the test solutions of Sample B and Sample C at an M/S ratio of 0% have the same color and concentration as their test solutions at an M/S ratio of 10% through visual inspection, and no suspension was observed. Hence, their photos are omitted. Here, the yellowish-brown color of

the test solution of Sample B and Sample C may be attributed to the formation of aqua complexes⁷⁰⁾ of chromium, iron, and others. Aqua complexes are large atomic groups formed by the binding (coordination bond) of water molecules to the metal atoms that serve as the core in an aqueous solution. In particular, when the core heavy-metal atom is a transition element, the aqueous solution is known to have a beautiful color⁷¹⁾.

Hexavalent chromium (Cr(VI)), which is the subject of immobilization in this study, is an element belonging to the transition metals and is known to form aqua complex ions such as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ by coordinating with six water molecules in aqueous solution, resulting in a yellowish-brown color. Since Samples used in the experiment in this section were from the soil generated during tunnel construction, the arsenic, hexavalent chromium, and lead are thought to be naturally derived. In particular, chromium is known to exist considerably in nature as trivalent chromium than as hexavalent chromium. Based on these facts, the color of the test solutions may have been affected by the aqua complex ions derived from trivalent chromium.

On the other hand, iron is not a specific hazardous substance and is not the subject of immobilization in this study. However, like chromium, it is an element belonging to transition metals and exists as an aqua complex ion such as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, which is coordinated with six water molecules, and is known to cause the test solution to turn yellowish-brown. Iron is also the transition metal most abundant in average soil, ranking 4th in Clarke number⁷²⁾, and is contained in average soil at 4.7% by mass. Chromium and lead, which are the subjects of immobilization in this study, are ranked 21st and 36th in Clarke number, with Clarke numbers of 0.02% and $1.5 \times 10^{-3}\%$, respectively. Lead does not belong to the transition elements. Based on these facts, it is presumed that the yellowish-brown color of the test solutions was most likely due to the formation of iron aqua complex ions.

Therefore, it is clear that the immobilizer used in the study in this section has the function of adsorbing yellow-brown aqua complex ions and similar substances, turning the test solutions colorless and transparent. Additionally, by increasing the M/S ratio up to 40%, the immobilizer reduces the leaching concentrations of heavy metals such as arsenic, hexavalent chromium, and lead to levels below the soil environmental standards. We believe that this conclusion is primarily attributed to the adsorption action of ettringite and similar compounds



(a) M/S=10%

(b) M/S=20%

(c) M/S=40%

Photo 2: Colors of test solutions made from specimens of Sample B⁶⁴⁾



(a) M/S=10%

(b) M/S=20%

(c) M/S=40%

Photo 3: Colors of test solutions made from specimens of Sample C⁶⁴⁾

formed by the composite recycled material used as the immobilizer in this section of the study.

6. Conclusion

Limestone is a mineral resource that Japan can self-sufficiently produce. It is inexpensive due to its vast reserves, physiochemically stable, and harmless to humans and animals. Consequently, it has been used in a variety of fields, including agriculture, construction, civil engineering, steel, cement, and food, for a long time. Quicklime (CaO : calcium oxide) is produced by calcining limestone (CaCO_3 : calcium carbonate), and slaked lime ($\text{Ca}(\text{OH})_2$: calcium hydroxide) is obtainable by adding water to quicklime. These are used in a variety of ways depending on their characteristics and applications.

As mentioned in this paper, calcium carbonate and calcium hydroxide are used as neutralizing agents for flue gas desulfurization. The flue-gas-desulfurization gypsum produced by this process is reused as a raw material for gypsum boards. Eventually, waste gypsum boards that have completed their role as building materials are reused again as agricultural fertilizers and soil improvement materials, returning them to the soil. In this way, lime is an excellent mineral usable in a cascade manner at multiple stages. Calcium oxide (CaO), indispensable for the synthesis of ettringite in composite recycled materials made from industrial by-products, is derived from blast-furnace slag. Its roots go back to limestone.

Meanwhile, in modern society, attention has been paid to efforts to solve problems such as reducing greenhouse

gas emissions, making effective use of resources (e.g., through the 3R: Reduce, Reuse, Recycle), and rational use of energy (e.g., improving exergy and energy efficiency).

The composite recycled material that we have been engaged in this study for development can be considered to be an extremely excellent material based on these perspectives. Industrial by-products such as waste gypsum board, coal ash, and blast-furnace slag are effectively used as materials for composite recycled materials. However, it has been revealed that when these materials are used alone, fluorine, hexavalent chromium, cadmium, lead, and other substances are leached in amounts exceeding the soil environmental standards. In response to these facts, this study has demonstrated that by mixing these industrial by-products in the composite recycled material in a chemically equivalent manner that maximizes the production of ettringite, the material not only immobilizes the heavy metals it contains, but is also effective in immobilizing high concentrations of heavy metals that are several tens of times the environmental standard.

In conclusion, this composite recycled material is believed to be an extremely excellent material that has the effectiveness as a solidification agent based on hydraulic bassanite, as well as the ability to immobilize heavy metals.

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