USE OF PAPERMAKING SLUDGE AS NEW MATERIAL

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ABSTRACT: Recent efforts to actively recycle paper have caused the amount of papermaking sludge to increase steadily each year, with current estimates of over 3,000,000 tons discharged annually throughout Japan. The Nippon Telegraph and Telephone Corporation has achieved success in converting ash derived from incinerated papermaking sludge into a new porous material with high cation exchange capacity by reacting this ash in an alkali solution. This paper reports some application of the new material to environmental conservation, such as improvement of water quality and admixture in concrete.

INTRODUCTION

Today, materially-abundant Japan is overflowing with durable consumer goods such as automobiles and home appliances, with considerable diversification in materials ranging from foodstuff and clothes to paper. For instance, the number of automobiles in the country rose to 6,685,000 in 1995, accounting for a share of 10% of all the automobiles in the world, and ranking second only to the United States. The diffusion rate of consumer appliances such as color television sets, air conditioners, refrigerators, and washing machines is nearly 100%.

The production volume of paper and plastics used in daily-life activities has also increased. The annual consumption of plastics per person was 90 kg, and the annual consumption of paper per person was 239.1 kg in 1995. The enormous volume of waste products generated as a result is unavoidable in such a high-consumption society (Makino 1998).

A general observation of the material balance in Japan in 1995 shows that of the 2,360,000 tons of material resources used, 1,350,000 tons were newly accumulated as a result of economic activities, 800,000,000 tons were discarded as waste, and the amount of recycled resources amounted to no more than 210,000,000 tons (Environmental 1996).

For reducing the waste generated, so-called 4RE (reduce, recycle, reuse, renewable) technological developments are required. This paper discusses the material recycling of resources with focus on the recycling of papermaking sludge during the papermaking process.

The volume of papermaking sludge generated during the papermaking process varies depending on the type of paper produced, but generally about 30% of the sludge is incinerated to ash and disposed of in sanitary landfills (Fig. 1). This ash is a residue of ignition loss, which filled up with kaolinite and calcium carbonate, serves as a cosmetic used as filling material to provide a smooth paper surface during the papermaking stage. The possibility of using this ash as a new resource by hydrothermal synthesis is also investigated in this paper.

REUSE OF PAPERMAKING SLUDGE

Up to now, various techniques for recycling resources have been used, such as utilizing ash derived from incinerating papermaking sludge, in filling materials such as asphalt and rubber, or as a material for manufacturing cement. However, this recycling is limited to a very small part, and most of the paper sludge has been used for sanitary landfills and is thus not effectively utilized (Working 1994). Active recycling of old paper, in the future, will help to protect paper resources, but one issue that will surface is the disposal of papermaking sludge.

Since the enactment of the NTT's Global Environment Charter, defined in November 1991, the Nippon Telegraph and Telephone Corporation (NTT) has been developing various technologies to reduce the volume of industrial waste generated by effectively reusing papermaking sludge. These include drying of granulated sludge, using it together with mud for the construction of communication tunnels, and using papermaking sludge as a material for improving soil properties, such as improvement in properties of weak, sandy soil generated during building works. These techniques make use of the properties of pulp fiber, a component of the papermaking sludge, in absorbing excess water in soil, and enhancing the bonding force between soil particles by bridging these soil particles.

In addition to pulp fiber, papermaking sludge contains very small quantities of minerals, such as kaolinite and calcium carbonate, used as coating agents for ensuring a smooth paper surface. The quantity of coating agents varies depending on the type of paper, but is generally between 5 g/m^2 to 20 g/m^2 (Editing 1985). When paper sludge is incinerated at temperatures in the range of 1,223–1,373 K, these minerals appear as incinerated residue (ash). It is known that ash exists mainly in the form of glass (amorphous) because it melts during incineration. Correspondingly, the incinerated ash may be considered to be amorphous aluminum silicate containing impurities. It is also known that when amorphous aluminum silicate contained in volcanic ash reacts with an alkali, it crystallizes and changes to a mineral called zeolite. In the present study, the ash from incinerated papermaking sludge was dissolved in an alkali solution and subjected to hydrothermal synthesis reaction. It was confirmed that the ash can be converted to a porous material after specific treatments. This new material has minute pores from nano- to milli-size. Therefore it was named microporous material (MPM) (Fig. 2). Approximately 60% by

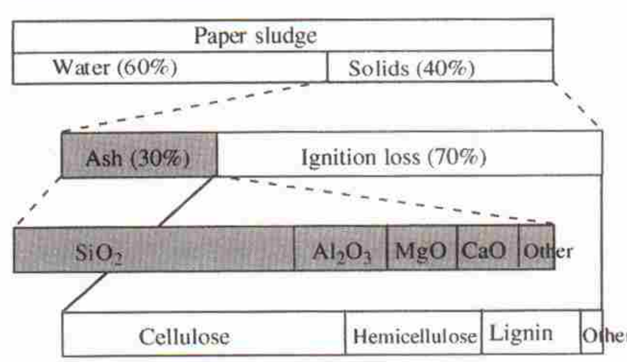

FIG. 1. Schematic Composition of Paper Sludge

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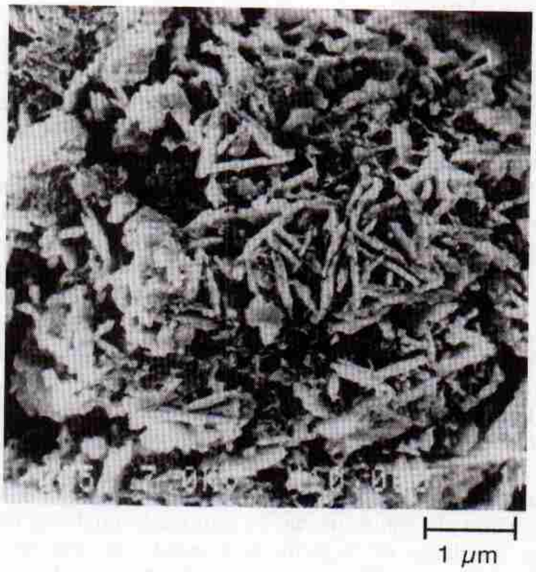

FIG. 2. SEM Photograph of MPM

weight of the destroyed papermaking sludge ash represents zeolite, such as sodalight or phillipsite, after the hydrothermal synthesis reaction. It may be said that MPM is zeolite including calcium carbonate. The zeolite group exhibits cation exchange behavior, and can absorb and exchange certain cations. Also, calcium carbonate reacts with phosphoric acid to form phosphoric acid calcium (apatite). This calcium carbonate can adsorb and remove the phosphoric acid ion that zeolite cannot adsorb when it is used as water purification materials. MPM also has a relatively large specific surface area and can be formed into various shapes. Some applications of MPM are described in the following sections.

USE AS ADMIXTURE FOR CONCRETE

In the last few years, acid rain has been an environmental issue affecting the ecosystem. Fortunately, Japan has not been damaged as much as Europe and America, because the soil in Japan is acid soil and the microorganisms possess a certain degree of resistance. However, so-called "acid rain icicle" has started to damage concrete structures. There are two types of acid-rain generating mechanisms. In the first mechanism, the carbon dioxide in the atmosphere dissolves in rain and when it reaches a saturated condition, the pH becomes 5.6. In the second mechanism, when gases other than carbon dioxide, such as sulfur oxide (SO_X) and nitrogen oxide (NO_X) are discharged into the atmosphere, they flow and disperse in the atmosphere, decomposing ozone (O_3) molecules and forming active oxygen atoms. These oxygen atoms react with the water vapor to form hydroxyls (HO). HO converts SO_X to sulfuric acid (H_2SO_4) and NO to nitric acid (HNO_3). In addition, hydrogen peroxide (H_2O_2) dissolved in water in clouds reacts with SO_X generating sulfuric acid. These acids form either dry fallout when they fall directly on the earth's surface or wet fallout when they are included in rain, fog, or snow. The latter is called acid rain or acid snow (Nakanishi 1994).

The acid resistivity of concrete is about pH 4 to pH 5. Sulfuric acid, in particular, reacts with the suspended calcium hydroxide in concrete, forms calcium sulfate (dihydrate of gypsum), and causes expansion of the volume of concrete. Furthermore, this calcium sulfate and tricalcium aluminate react, forming ettringite. This ettringite has a high volume expansion rate and causes the concrete to deteriorate and collapse.

Tests were carried out to confirm the effect of MPM in inhibiting damage to concrete by using MPM as cement admixture.

Test pieces were prepared using cement mortar made of ordinary portland cement and river sand, and MPM-mixed cement mortar made by substituting 5, 10, and 15% of ordinary cement by MPM. Artificial acid rain was sprayed on the test pieces and accelerated deterioration tests were carried out. Artificial acid rain was prepared by mixing SO_4^{-2} (1.25 ppm) and NO_3^- (2.58 ppm) in a ratio of 1:2. Taking the annual precipitation in Japan as 1,800 mm, an amount equivalent to the precipitation for 10 years, was continuously sprayed on the test piece. Considering the average weather conditions of Japan, the test cycle used was as follows: an 8-h spraying of artificial acid rain on the test piece, followed by a 4-h drying

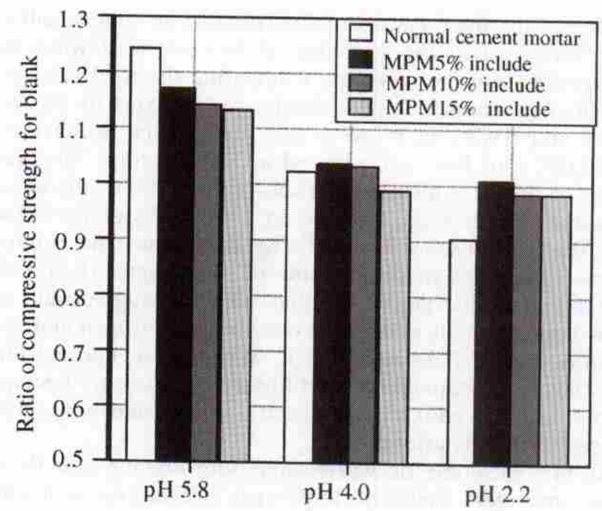

FIG. 3. Unconfined Compression Tests (10 Years of Rainfall)

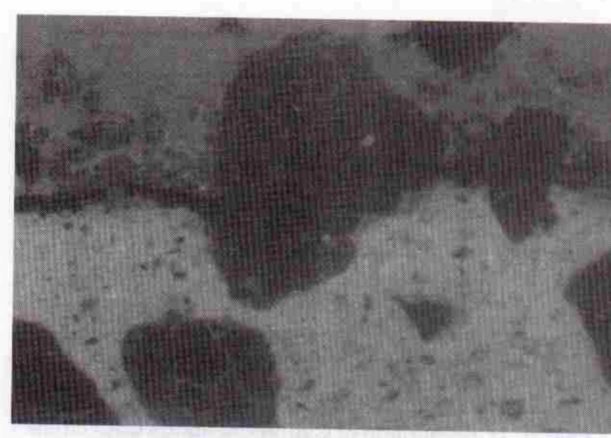

FIG. 4. Portland Cement Mortar (pH 2.2)

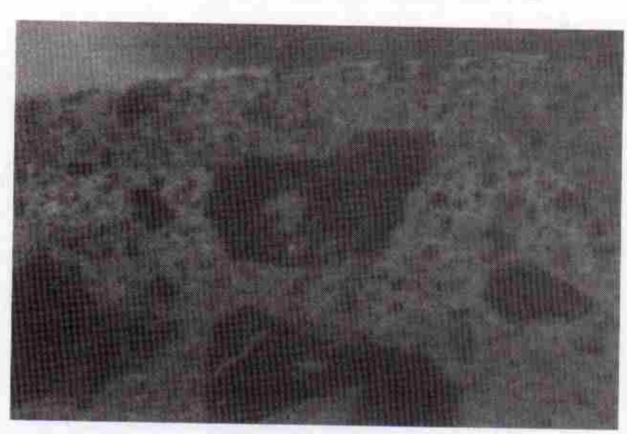

FIG. 5. Portland Cement Mortar Containing MPM (pH 2.2)

period wherein the test piece was exposed to the rays of an ultraviolet lamp, and, finally, a 12-h blank period to allow the test piece to dry.

Fig. 3 illustrates the results of uniaxial compression strength tests carried out after the acid rain tests. Figs. 4 and 5 show a surface section of the test piece after its treatment by fluorescent agents (the methyl meta-acrylate) method developed by Nishiyama et al. (1990). It is seen that ordinary cement mortar is affected by artificial acid rain, but when 5–10% of cement is substituted by MPM, the cement mortar remained unaffected.

USE OF MPM AS A WATER QUALITY IMPROVEMENT MATERIAL

One of the main causes of deterioration in water quality of lakes and rivers is the discharge of domestic wastewater from households into these waters. Comparing the total amount of biochemical oxygen demand discharged in rivers for the years 1970 and 1989, it is seen that the annual discharge of 3,750,000 tons has been reduced to 780,000 tons. The breakdown of this amount for 1970 shows that 80% of the amount was due to industries, whereas in 1990, 74% of the amount was due to households, indicating that almost no improvements have been made to domestic wastewater (Ishi 1992). Water that is discharged together with cooking residue contains large amounts of highly-concentrated nitrogen and phosphorous material dissolved in it. When these nutrients flow into lakes, phytoplanktons proliferate, lakes start becoming turbid, and an anoxic state occurs at the lake beds, which causes further deterioration.

To prevent domestic wastewater from flowing directly into lakes and rivers, measures to prevent discharging such wastewater and provision of sewage systems are necessary. However, provision of sewage systems requires an enormous amount of capital and time. The writers therefore started research in 1997 related to improving domestic wastewater using MPM and existing wastewater discharge channels and other collection catch basins.

MPM has adequate properties as a water quality improvement material, which can be seen in Figs. 6 and 7, showing comparisons of the cation exchange capacity and the specific surface area of materials used to improve water quality, such as activated charcoal and natural zeolite. The effect of removal of nitrogen and phosphorous by MPM was verified using water of a river streaming into Teganuma in Chiba Prefecture, which was made to flow in test channels (2 channels each, 10 m in length) (Figs. 8 and 9). Teganuma is one of the most polluted lakes in Japan, with chemical oxygen demand of 24 mg/L.

The results of tests showed that more than 51% of total nitrogen and phosphorous can be removed, satisfying the water quality standards of Teganuma. Considering the water permeability and simplifying the tests, MPM was shaped in the form of balls (6.5 cm in diameter) after granulation. For practical applications, it may be necessary to shape MPM into concrete panels and so on, but it has been proven that MPM can adsorb nutrient salts dissolved in water.

Studies were also carried out to confirm whether MPM, af-

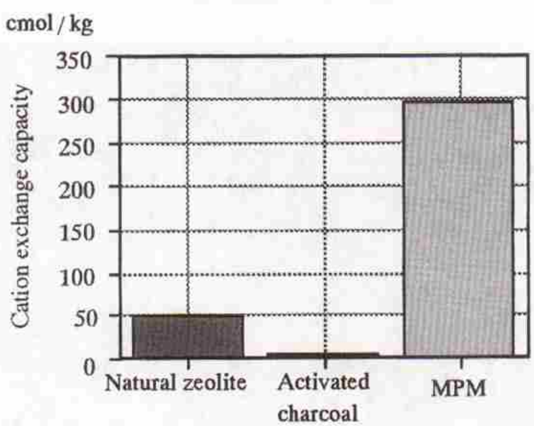

FIG. 6. Comparison of Cation Exchange Capacities

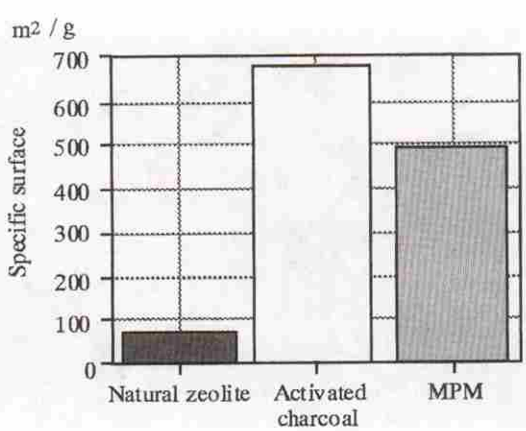

FIG. 7. Comparison of Specific Surface

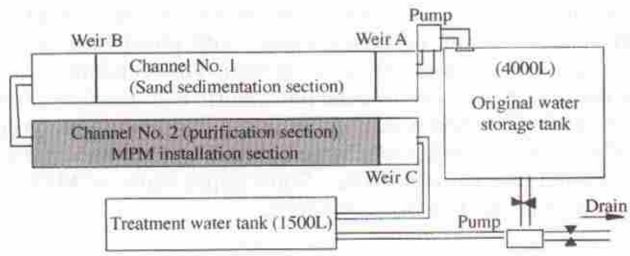

FIG. 8. Experimental Channel Facilities

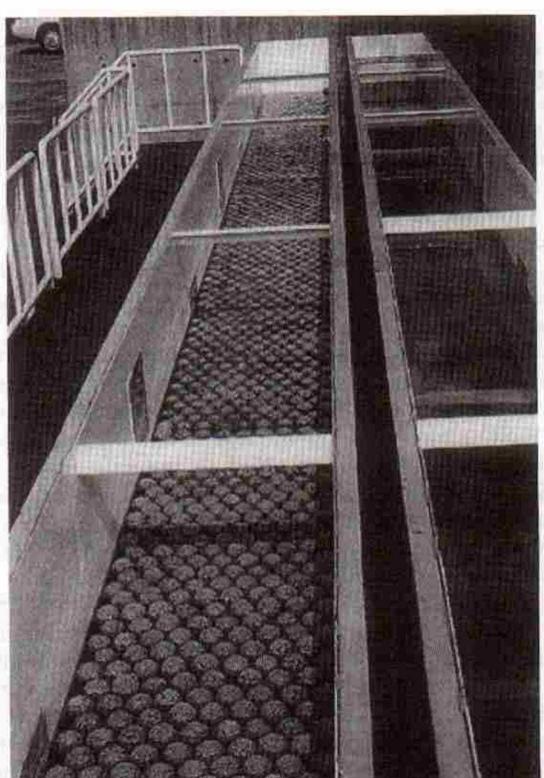

FIG. 9. Experimental Channel

ter adsorbing nitrogen and phosphorous in the tests, could be reused as borrow material after mixing it with soil. Borrow material for cultivation of plants is being used in vegetation work accompanying building and construction works. Large quantities of earth are being excavated from mountains or agricultural land and used as borrow material, and about 1,000,000 m^3 of natural soil is being lost (Nishiyama et al. 1990). It has been verified through growth tests on corn that MPM assists vegetation growth when it is mixed with soil. Moreover, MPM has buffering ability and water retentivity, and is considered to be effective in preventing the acidity of soil due to acid rain and in preventing water shortage in metropolitan areas.

CONCLUSIONS

The conclusions related to the use of MPM obtained by hydrothermal synthesis reaction of ash obtained by incinerating papermaking sludge are as follows:

1. Although issues such as effective arrangement of MPM remain to be solved, it has been proven that MPM can remove nutrient salts such as nitrogen and phosphorous dissolved in water. Particularly, the removal rate of phosphorous, which has been limited up to now, is close to 50% using MPM.
2. After improving the water quality, MPM can again be reused as a complement of borrow material for vegetation, enabling total recycling to be achieved.
3. MPM enhances the acid resistivity of concrete when used as an admixture in concrete.

This paper researched the use of MPM as a water quality improvement material and an admixture for concrete. However, in addition, MPM can also be used to absorb gases such as formaldehyde, the cause of the Sick House Syndrome, which is a problem in highly air-tight and highly-insulated residences. Research on this topic is in progress. The utilization methods and formats of MPM are likely to become a topic of future studies.

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