Sewage Sludge Carbonizing System and Properties of Carbonized Products

Takashi Mori
Hakuei Yamamoto
Research and Technology Development Division
Japan Sewage Works Agency
5141 Shimosasame, Toda, Saitama, 335-0037, Japan
mori07@jswa.go.jp
hakuei@jswa.go.jp

ABSTRACT

Carbonized products derived from organic sewage sludge are attracting attention as a novel material with possibilities for various utilization because of similar in properties to that of charcoal. Up to now, the sewage sludge has been disposed after dehydration, and also the incinerated ash of it has been utilized as feedstocks of Portland cement and construction materials. These utilizations, however, has no growth potential in the future.

In this paper, the carbonization system of sewage sludge, properties of its carbonized products and utilization methods are described. The materials are expected as new utilization forms, because of their characteristic properties such as high porosity, low density, highly absorptive capability and so on. The soil conditioner, dehydrating auxiliaries and deodorizer are studied as effective utilization candidate.

KEYWORD

Utilizations, Carbonized

CARBONIZATION PROCESS

Figure 1 and 2 show structure of carbonization furnace and flow sheet of carbonization system, respectively.

Three types carbonization furnaces are used in the experiment, that is, external heating type rotary kiln, external heating type screw kiln and internal heating type rotary kiln.

Charge after drying or direct charge is adopted as the feeding procedures. In the case of the external heating kiln, the sludge is supplied to a rotary dryer and dehydrated at 700 ℃ with hot gas from the air furnace. After the water content of the sludge in the dryer is

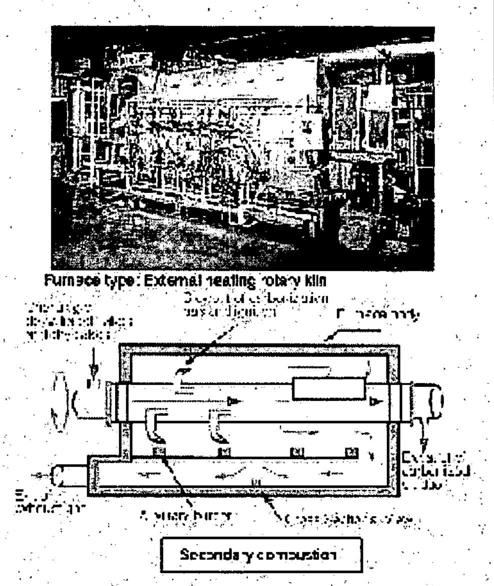


Figure 1 Structure of Carbonization furnace
Note : The sludge that was adjusted to contain approx. 40% of water in the drying furnace is baked in the retort at 700℃

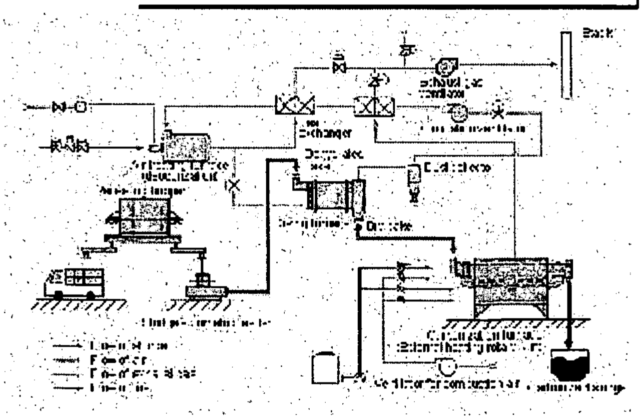


Figure 2 Flow Sheet of Carbonizing System
Note :The main system consists of a hot air furnace, a dryer and a carbonization furnace.

reduced to 40%, it is introduced into the carbonization furnace. The carbonization furnace contains a retort (rotary kiln), in which the sludge is carbonized at high temperature with shutting off the air. Exhaust gas treatment for oxidative degradation of generating odor and decomposition of residual substance are carried out in the external heat chamber, in which temperature keeps at a certain level. The retort rotating at 2-3rpm conveys the sludge to the rear end in 20 to 30 minutes. The carbonization gases such as methane, ethylene and carbon monoxide generated from heat- treated sludge are utilized as fuel of the resort.
The carbonized materials produced by carbonizing operation in reduction condition at high temperature possibly generate heat by oxidation if it is exposed in the air.
To avoid this phenomenon, the heated materials are indirectly cooled to the room temperature and then stabilized by water humidification before utilization.

PROPERTIES OF CARBONIZED PRODUCTS

1. Reduction of weight by carbonization of organic sewage sludge

Figure 3 shows weight change of water, organic substance and ash during carbonization process. 100-weight part of dehydrated cake is reduced to 25.7 and 5.8 weight part through drying and carbonization process, respectively. Namely, carbonization process reduce the volume of dehydrated sludge with 83 % water to 1/18. During the carbonization process, approximately 80% of organic substance in the sludge volatilizes as gas through carbonization and the remaining substance of approximately 20% is immobilized in the carbonized products.

Almost oxygen and hydrogen in the dehydrated sludge gasify through carbonization and approximately 70% of carbon, which is main element in dry solid substance, also gasifies but 30% of it remained in the carbonized products. The selective immobilization of carbon through carbonization is also confirmed by the fact that the carbon content of the organic substance in carbonized products accounts for approximately 80% which is higher value compared with those of dehydrated and dry cake as shown in Figure 4.

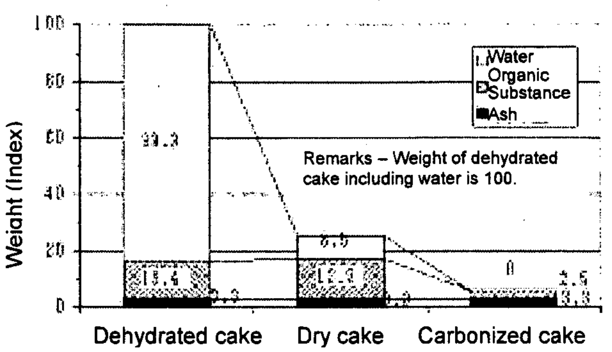


Figure 3 Weight Change of Sludge by Drying and Carbonization Treatment

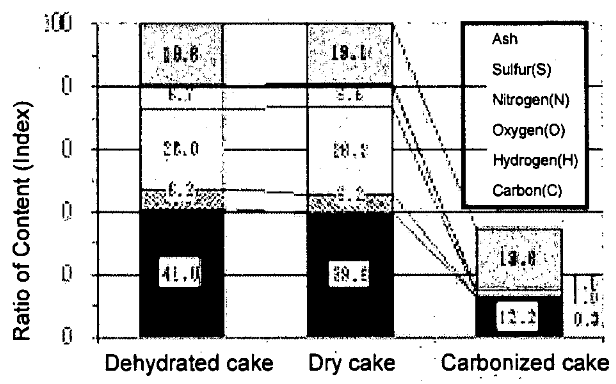


Figure 4 Change in Ratio of Content of Organic Substance by Drying and Carbonization Treatment

Note: The moisture percentage of dehydrated cake is reduced to approximately 6% from 80% by carbonization treatment.

2. Physical Properties of Carbonized Products

The typical physical properties of the carbonized products are shown in Table 1. Activating treatment increases specific surface of charcoal. Compared with normal charcoal and activated charcoal, the average pore radius of carbonized products is similar to those of normal charcoal and 5 times as big as the activated charcoal, partially because no activating procedure is applied to the products. The total pore volume of the products is less than half of that of the activated charcoal. The specific surface area of the products is almost same as that of normal charcoal, and less than 10% of the activated charcoal. The bulk density is as light as 0.35 to 0.59. Although the total calorific value is 12 to 13 MJ/kg, which is equivalent to that of charcoal (30 MJ/kg)

Thus, in view of the fact that the properties of carbonized products are considerably similar to those of charcoal, the application to soil conditioner and deodorizer can be considered as effective utilization.

Table 1 Physical Properties of Carbonized Products

	Unit	Carbonized Products	Reference	
			Charcoal	Activated Charcoal
Water	%	1.78	1～2	1～5
Ash	%	42.0～57.8	9～15	1～5
Volatile Component	%	5.57		
Bulk Density		0.3～0.59		
Specific Surface Area	m^2/g	23.2～114.2	50～400	Approx. 1000
Total Pore Volume	ml/g	0.062～0.122	0.05～0.1	0.46
Average Pore Radius	Å	53.5	37～6500	8.5～10
Carbon	%	23.9～36.17	98	90～98
Nitrogen	%	1.9～5.33		
Hydrogen	%	0.62～2.86		

Note: The carbonized product is a material having a specific surface area and pore volume similar to those of charcoal.
Its carbon content is about 40%, which is smaller than that of charcoal.

3. Content of Metal Element

All tests on both elution of heavy metals and content of six elements, including total mercury, of the products reveal to meet the standard values designated under "Fertilizer Control Low". "Administrative Standard with Regard to the Prevention of Accumulation of heavy Metals etc. in the Soil for Agricultural Land" states that the concentration of zinc in the soil should be kept below 2.5 to 3 times through the carbonization of dehydrated sludge resulting the decrease of organic substance content, for application of the carbonized products to agriculture. Careful attention should be made to mixing ratio with the soil, so that they are used within the administrative standard.

UTILIZATION OF CARBONIZED PRODUCTS

Effective utilization of carbonized products taking advantage of its properties is being lead for soil conditioner in green farms, dehydrating auxiliaries, deodorizer, compost additive and snow melting agent.

1. Uses in Green Farms

The following are vegetable and flower cultivating experiments results conducted to investigate the applications to green farms.

Properties for Application to Green Farms

Chemical Properties

Studies have been conducted on three different types of carbonized products, which were derived from different amount of polymer-dehydrated sludge as shown in Table 2. "Soil Subcommittee of Japanese Institute of Landscape Architecture" recommends as vegetation soil that PH is alkalescent because for improvement of acid soil. Electric conductivity (RC) is an index indicating the concentration of the salts in the soil. Small EC value of products means that concentration of salts in the products is low and has no recognizable harm to plants. The positive ion exchange capability is an index indicating the ability of soil particles to absorb nutrition salts (Fertilizer remaining ability).

No particular effect has been observed in this respect by mixing carbonized products. However, carbonized products have physical absorption ability in addition to chemical absorption, and they showed effective fertilizer retaining ability in the actual experiments on plants

It was found that the sewage sludge carbonized products contain phosphor in a form which plants easily absorb. This is the unique property of the products that is not in other sludge materials.

The other value described in Table 2 are within the range desirable for vegetation soil, therefore, the improvement of the soil can be expected by mixing carbonized products with the soil.

Table 2 Chemical Properties of Carbonized Products (for Application to Green Farms)

	Unit	Carbonized Product 1	Carbonized Product 2	Carbonized Product 3	Soil Standard
pH		7.9	7.1	7.5	4.5~8.0
Electric Conductivity	s/cm	0.16	0.20	0.15	1.0>
Positive Ion Exchange Capability	cmol/kg	5.6	6.8	7.5	6<
Phosphate in Available Form	$mgP_2O_5/100g$	150	54	150	10<
Phosphate Absorbing Factor	$mgP_2O_5/100g$	240	—	110	1000>

Note: The carbonized product is alkalescent and has excellent water permeability. It contains phosphor in abundance in a form that can be easily absorbed by plants, one of the features of sewage sludge carbonized products.

Physical Properties

Table 3 shows the results of analysis on the physical properties of carbonized products, the soil and products/soil mixture. It is said that the desirable coefficient of standard water permeability of the soil for plant cultivation is 10-4 cm/s and above. The farmland used in this experiment of vegetable cultivation had rather poor water permeability coefficient in the order of 10-5 cm/s. The coefficient was improved to 10-3 cm/s order by mixing carbonized products with the farmland soil by 30%. The suitable ratio of gaseous phase in the triphase distribution is 13 % and above for farmland. The gaseous phase ratio of the soil was raised to 21% from 8.9% by mixing carbonized products by 30%. Further, the effective water retaining volume was improved to as high as 100 l/m3 from 66 l/m3

Table 3 Physical Properties of Carbonized Products and Soil
(For Application to Green Farms)

		Unit	Carbonized Product	Soil	Mixed Soil*
Coefficient of Saturated Water Permeability		cm/s	—	1.3×10^{-5}	2.0×10^{-3}
Triphase Distribution	Solid Phase	vol%	24.7	45.8	39.3
	Liquid Phase	vol%	38.9	45.3	39.3
	Gaseous Phase	vol%	36.4	8.9	21.4
Effective Moisture	pF1.8～3.0	l/m3	100	42	66

* : Soil was mixed with carbonized products by 30%.

Note: By mixing carbonized products with the silty soil, the gaseous phase portion has increased, and as a result, the soil has been improved to provide an environment suitable for culture.

Examples of Utilization

(1) Application of the carbonized products to Carrots, Chinese Cabbages (Konatsuna) and Kidney Beans cultivation

In order to study the effect of the soil improvement, the farmland was plowed to depth of 15 cm and carbonized products were mixed with the soil at the ratio of 0%, 10% and 30%. Then, the cultivation experiments have been conducted on carrots, Chinese cabbages and kidney beans. In the experiment of carrots, the higher the carbonized products mixing ratio increased, the heavier the total and substance portion weight became. The results show that the carbonized products are believed to have contributed to the improvement of physical properties and the fertilizer retaining ability of the soil.

On the other hand, in the case of Chinese baggage, the higher the mixing ratio of carbonized products was, the lighter the weight of surface portion was, the bigger the ratio of subsurface portion to the entire plant. These differences occur characteristically to vegetable plants when the nutritious substances are supplied slowly and effectively. It is believed that the difference is taken place because the nutritious salt is temporarily absorbed and retained by the carbonized products, and as a result, the fertilizing effect in the soil changed to slow and effective pattern. The beans family such as kidney beans is generally capable to absorb nitrogen from the root nodules formed at the root in symbiosis with a microorganism having the ability of immobilizing nitrogen (ability to immobilize the nitrogen in the air for utilization as a nutrient)

The higher the mixing ratio of the carbonized products was, the heavier the weights of subsurface portion and the root nodule were. The results show that the carbonized products contributed to improvement of air permeability.

The pore structure and chemical properties of the products are believed to be suitable for the multiplication of the symbiotic microorganism (Table 6).

Table 4 Weight of Carrot by Organ, S/R Ratio* and Yield Index

	Weight of root portion, raw state (g)	Weight of root portion, dry state (g)	Weight of surface portion, raw state (g)	Total weight, dry weight (Physical weight) (g)	S/R Ratio	Yield Index
Control	141.4	14.22	5.56	19.78	0.391	100
C10%	164.4	15.34	6.52	21.85	0.425	116
C30%	177.2	17.49	7.40	24.89	0.423	126
Calcium Carbide	134.9	-	-	-	-	96

* : S/R Ratio means the ratio of the weight of surface portion to the weight of subsurface portion. The more abundant the nutrient in the soil is, the higher S/R is.

Table 5 Height, Surface and Subsurface Weights, and S/R Ratio* of Chinese Cabbages

	Height (cm)	Weight of Surface Portion(g)	Weight of Subsurface Portion(g)	Physical Weight(g)	S/R Ratio	Yield Index
Control	25.7	1.736	0.111	1.847	15.7	100
C10%	26.7	1.519	0.101	1.620	15.7	88
C30%	24.8	1.423	0.114	1.537	12.5	82

Table 6 Weights of Root Nodule and Subsurface Portion (Average Weight per Plant, grams in Dry State)

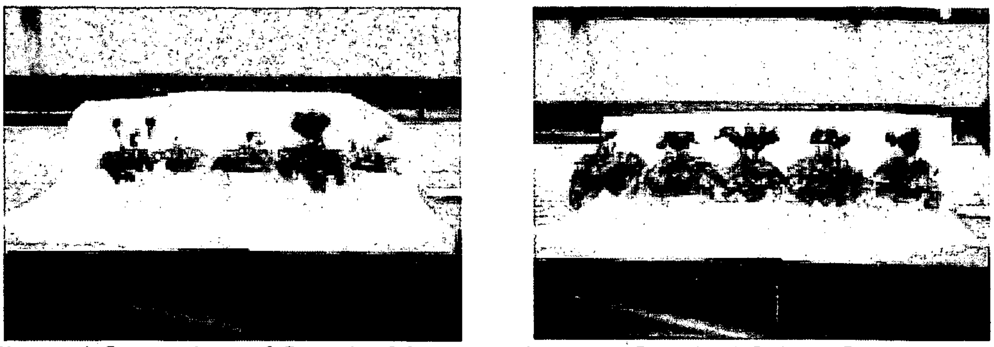
	Weight of Root Nodule (g)	Weight of Subsurface Portion (g)
Control	0.0002	0.349
C10%	0.0044	0.447
C30%	0.0077	0.488

(2) Culture Experiments on Cyclamen

The experiment in the past confirmed that the use of carbonized products in the soil for stock and antirrhinum cultivation resulted in increase in weight of total plant as well as individual organs, compared with pearlite which is used as air permeability agent, and also the proper mixing ratio of carbonized products was 30% to 50%.

The cultivation experiment was carried out on cyclamen that requires a higher cultivation technology. As the result, it found that as far as the growth status before naturalization is concerned, the conventional method produces better results in both the withering ratio and growth rate than the case where the carbonized products is added. It is presumed that since there was no difference in the subsurface growth, the difference in withering ratio and growth ratio is due to the inability of the sprout to break the filler of the carbonized products.

The comparison of the growth both in the conventional soil and the modified soil after naturalization revealed that the number of flowers and flower weight were better than the conventional soil composition when the carbonized product was used as the cultivation medium. The test result confirmed that the carbonized sludge was also suitable for the soil for cyclamen cultivation (Picture1).



Picture 1 Comparison of Growth of Cyclamen between Standard Culture Soil (Left) and Carbonized Product Culture Soil (Right)

Chemical Bonding Form of Heavy Metals

The analysis on heavy metal forms was conducted for zinc, copper, nickel and cadmium employing a successive extraction method. Very little heavy metals in the exchanged state that are likely to elute were detected. The ratio of inorganic and organic coupling state was as small as about 5 to 7 wt %. The most part of heavy metals exist as free oxide and crystallized state which do not elute (Table 7).

Table 7 State of Heavy Metals in Carbonized Sludge

State	Unit	Zinc(Zn)	Copper(Cu)	Cadmium(Cd)	Nickel(Ni)
Exchangeable	mg/kg	1.0	<0.4	<0.2	<1
Metals Combined to Inorganic matter	mg/kg	93.4	53.6	<0.2	4.3
Metals Combined to Organic matter	mg/kg	1.1	<1	<0.5	<2.6
Metals Occluded by Free Oxide	mg/kg	73.3	174	<1	<5.2
In the Crystal lattices	mg/kg	1970	541	<0.5	65.5
Total	mg/kg	2139	769	<0.5	69.8

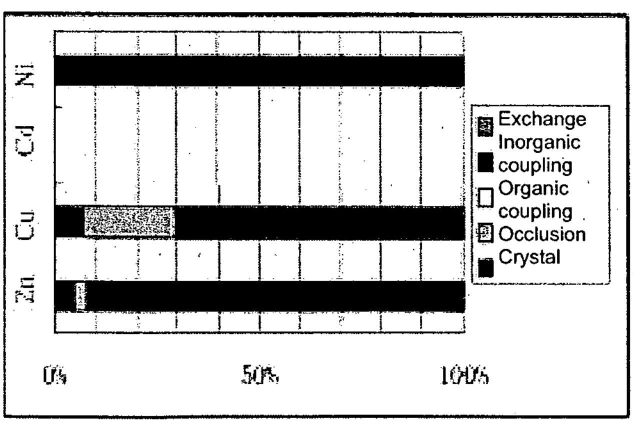


Figure 5 Retaining State of Heavy Metals in Carbonized Products

Note: Since more than 90% of heavy metals are retained in the crystal or occlusion state, the possibility of elution under the natural environment is very low.

2. Application to Deodorization

Since the carbonized product has similar pore volume to that of charcoal, its characteristic to absorb and remove odor ingredient is attracting attention. Since it is excellent ability to absorb hydrogen sulfide, the evaluation test as deodorizer was made in comparison with the activated charcoal. Breakthrough and absorption amount test of hydrogen sulfide was conducted using both the carbonized sludge and the activated charcoal.

The experiment was carried out by using PVC column in which the activated charcoal or the carbonized sludge was filled. Hydrogen sulfide was gone through the column. Concentration of sulfide was measured at the inlet and outlet of column. Thus, the relationship among the concentration of the original odor, the ratio of order removal and the breakthrough time were measured. Tables 8 and 9 show the properties of materials used in the experiment and test condition.

Table 8 Physical Properties as Deodorizer

Carbonized Product	Specific Surface Areas : 10～100m2/g Pore Volume : 0.01～0.1cc/g
Activated Charcoal	True Density : 2.1g/cc Particle Density : 0.75g/cc Filling Density : 400～470g/l Specific Surface Area : 1200m2/g Pore Volume : 0.86cc/g in Granule State

Table 9 Condition for Deodorization Test

Item	Requirements
Superficial Velocity (LV)	0.3m/sec or below
Contact Time (CT)	1.2 sec or above
Layer Thickness	36cm and 72cm
Concentration of Original Odor (H2S)	70, 100ppm

The relationship between contact time and breakthrough time, when the breakthrough point of an absorbing agent is set at the point where the concentration of exhaust gas reaches 5% of the original gas, is shown in Figure 6. The breakthrough time with the hydrogen sulfide of 100ppm concentration and the 2.54 sec. contact time was 60 min. for the activated charcoal and 27 min. for the carbonized sludge, respectively. In the case of 70ppm hydrogen sulfide concentration, the breakthrough time was 57 min. for the charcoal and 39 min. for the carbonized sludge. Namely, the breakthrough time for the carbonized sludge was about 1/2 of the activated charcoal. The filling volume of deodorizer and the total absorption volume of hydrogen sulfide at the breakthrough point of the deodorizer were measured, as shown in Figure 7. It was confirmed that the carbonized products have about 1/2 absorbing ability of the activated charcoal. While the absorption ability of charcoal was 40mg/100g, and that of the carbonized sludge was 20mg/100g. It is generally believed that the pore size distribution of activated charcoal greatly affects its odor absorption ability. Judging from the fact that the carbonized products, having about only 1/10 to 1/100 of specific surface and the pore volume compared with those of the activated charcoal, small amount contaminants such as iron and calcium are probably playing an important role in absorption ability.
In application of the carbonized products at the actual facility such as sludge storage tank, it is revealed that the absorption ability of carbonized sludge was about 1/3 of the commercial activated charcoal. In the future, use of the carbonized products of sludge as deodorizer in sewage treatment facilities etc. can be expected.

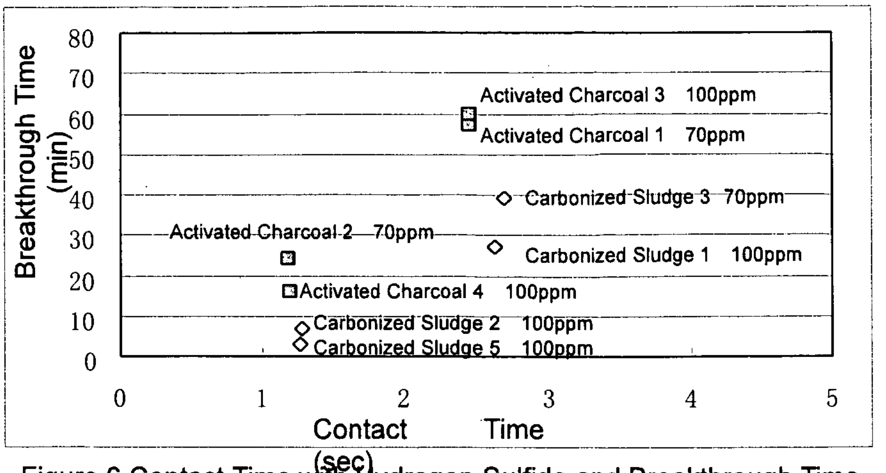


Figure 6 Contact Time with Hydrogen Sulfide and Breakthrough Time

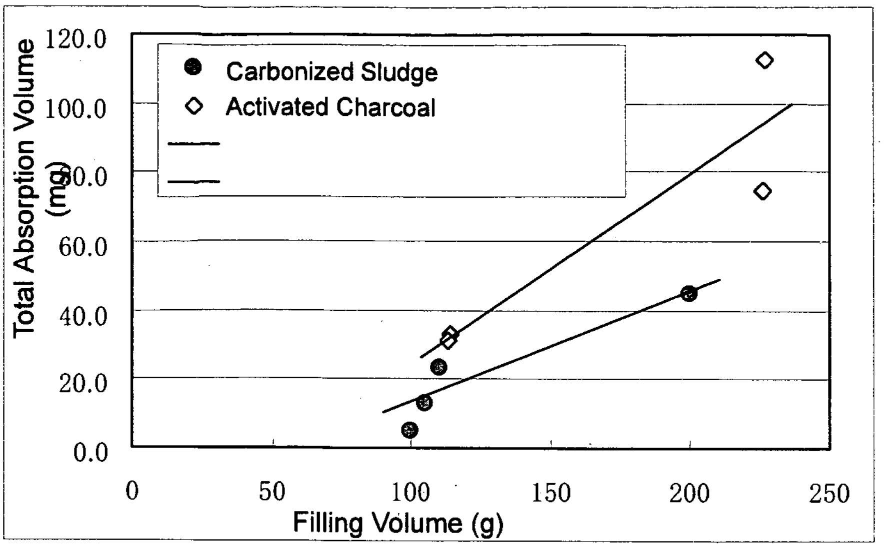


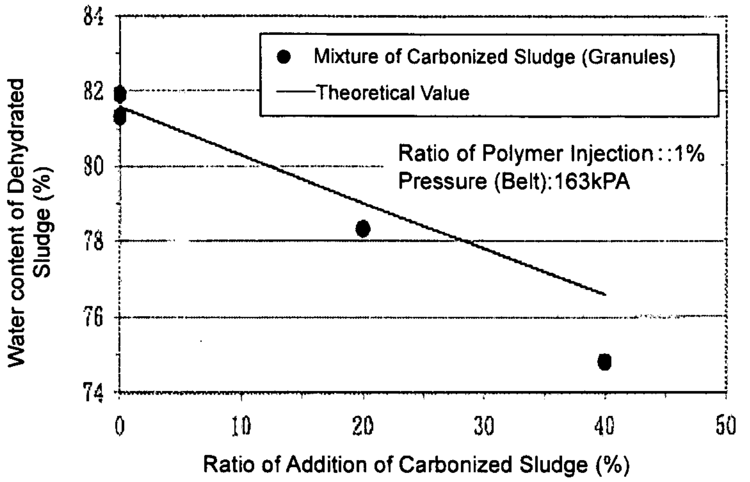
Figure 7 Total Absorption Volume of Hydrogen Sulfide on Activated Charcoal and Carbonized Products

Note: It has been confirmed that the carbonized products have approx. 1/2 to 1/3 of the total absorption volume of the charcoal on the market. They are particularly effective for sulfide gas odor.

3. Application to Dehydration

In the sewage treatment facility, cost reduction is an important item to be solved. In order to decrease the cost, dehydration is one of the key processes. A dehydration process using polymer coagulant and carbonized sludge as dehydrating auxiliaries for filter press already practically operates and gets the satisfactory results. This is the alternative method of ferric chloride-lime dehydration method.

Possibility of application to a belt press dehydrator, a filter press dehydrator and a centrifugal dehydrator is also examined. As equal to or less than the theoretical value water content was obtained with the addition of the carbonized products to the system, the application of the carbonized sludge to these type of dehydrator is also possible. Figure 8 shows the effect of addition of the carbonized product to the filter press dehydration process. Deviation of water content from the theoretical value was about 0.5% in case of addition of carbonized product by 20%, and 2% in addition by 40%. The experiment result suggests that the addition of the carbonized products to the dehydrated sludge as a dehydrating auxiliary has the positive effect and improve the dehydration capability, as result, can reduce the volume of sludge. Further, since the addition of the carbonized product reduces the water contents of the sludge down to 3 to 6%, the carbonized products is considered to have a lot of additional advantages in the after-treatment of dehydrated sludge such as combustion, melting and compost treatment



Note: By adding carbonized products, sludge cakes having a lower moisture percentage than theoretical value by 0.5 to 2% were produced. The carbonized product is presumed to have coagulation effect.

Figure 8 Effect of Addition of Carbonized Products in Belt Press Dehydrator

SAFTY INVESTIGATION

1. Exothermic Characteristic

Like as coal, the carbonized products has the exothermic or auto-ignition characteristic (Self-exothermic characteristic), when it is stored for long period time at a place with poor air permeability and thermal insulation. Since the self-exothermic phenomenon was observed in the storage hopper of carbonized products in the sewage sludge carbonization system, the intensive studies have been made to inspect its characteristics and safety measures. It was found that the sample easily generate heat, has fewer pore volume, low true density and great deal of volatile materials, this product is produced by insufficient carbonization. Accordingly, studies have been made with regard to the relationship between the extent of carbonization (refining ratio), the ratio of hydrogen and carbon (H/C), and the ignition temperature.

The test shows that the carbonized products with low refining ratio has high H/C ratio and active self-exothermic characteristic, and an low ignition temperature, approximately 200 ℃. Based on these facts, it became evident that the refining ratio can be an index of exothermic characteristic.

It has also been found that if calcium and aluminum exist in such forms as lime and aluminum oxide, they are hydrolyzed into calcium hydroxide and aluminum hydroxide, generating heat of hydration by water in the air. However, it has also been confirmed that temperature rise by humidification is relatively small and it will not be directly cause of heat generation and ignition of carbonized products. Further, it is also confirmed that the carbonization does not convert the heavy metal compounds into an unstable or easily oxidizable form, such as metal or carbide, and that the oxidation of metal compounds have little influence on heat generation of the carbon product.

Table 10 Ignition Temperature of Carbonized Products

	Specific Surface Area (m2/g)	Pore Volume (ml/g)	Ignition Temperature (Activated Charcoal Method)
Sludge Carbonized Product A	31.9	0.0853	327
Sludge Carbonized Product B (With Strong Exothermic Characteristic)	16.2	0.0597	261
Activated Charcoal Made from Coconut Husk	1,000～1,200	0.46	300
Charcoal	50～400		300～400
Coal	13～35	0.2～0.9	400

Note: Carbonized products derived from sewage sludge have different physical properties and ignition temperature depending on sludge conditions. The confirmed lowest ignition temperature is 261°C. It has been confirmed that they are likely to easily ignite compared with other carbonized products.

Table 11 Relationship between Carbonization Degree and Ignition

Sample	Ignition Temperature(°C)	Refining Ratio	H/C (Ratio of Number of Atoms)
Sewage Sludge Carbonated Product A	323	Below 1	0.142
Sewage Sludge Carbonated Product B	285	2.5	0.275
Sewage Sludge Carbonated Product C	295	3.1	0.27
Sewage Sludge Carbonated Product D	255	3.9	0.358
Sewage Sludge Carbonated Product E	200	8	0.620

Note: There is a correlation between the ignition temperature and the refining ratio, an index of the carbonization degree, and H/C. The lower the carbonization degree (i.e. high refining ratio and H/C value) is, the lower the ignition temperature is.

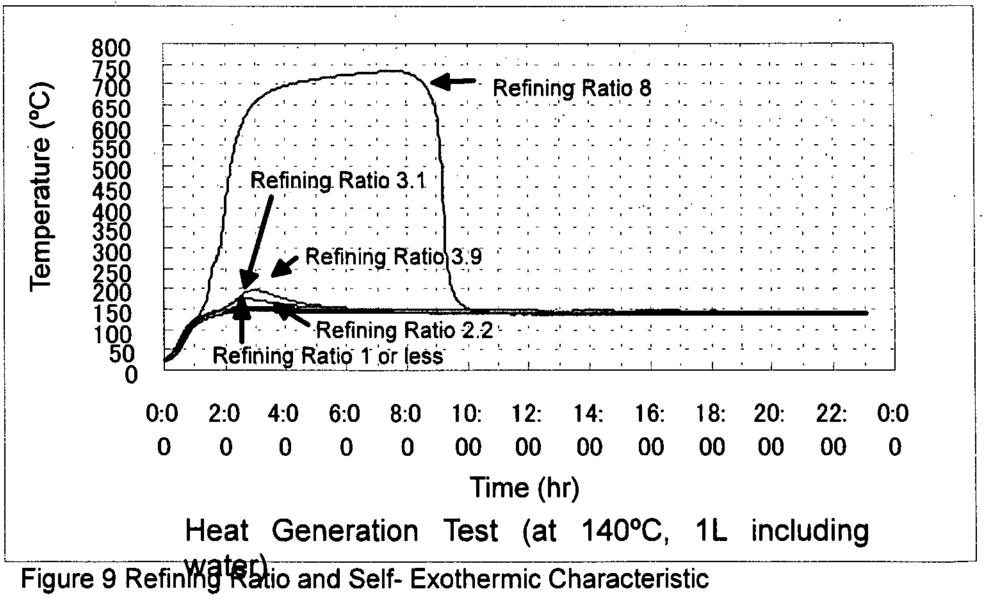


Figure 9 Refining Ratio and Self- Exothermic Characteristic

Note: The temperature of the carbonized product with the refining ratio of 8 considerably rose approximately 2 hours after the self-exothermic test. No temperature rise was found with the products having a refining ratio of 2.2, 1 and below.

2. Control of Self- Exothermic Characteristic

The test results on the self-exothermic characteristic of carbonized products are shown in Figure 9. It has turned out that the carbonized products having the refining ratio of 3.1 and above show the self-exothermic characteristic. The product of the higher refining ratio, i.e. the lower carbonization ratio generates more heat. The experiment on the self-exothermic characteristic was conducted for the carbonized products humidified with water by 30 to 40 % as countermeasure against heat generation. Temperature rise caused by self-exothermic reaction and hydration was suppressed by latent heat of evaporating water. However, at the same time, it was confirmed that the products with extremely insufficient carbonization occasionally show self-exothermic characteristic upon hydration and re-drying. Accordingly, the proper degree of carbonization for control of self-exothermic characteristic, and the stabilization of heat generation by humidification are essential for safe handling of the carbonized products.

CONCLUSION

The sludge treatment technology at the sewage facilities is undergoing a drastic change, from simple treatment to effective utilization of the products. Of various technologies that are being proposed for the effective utilization of sludge, the carbonization technology is the prospective method, because the carbonized products are expected to have effective applications.

When considering introduction of carbonization system, it is required to fully research the effective utilization, market and feasibility of the products. In order to use the sewer sludge effectively from now on, it is important to raise the quality of the products manufactured and that making sewage sludge into materials has the original feature, which changes that it is advantageous, becomes the business called for.

<Description of the refining index>

The refining index is the "t" of the electric resistance 10tΩ/cm. As the carbonization process advances, the electric resistance gets smaller, so does the value of " t" .

From the viewpoint of beneficial application, good carbonized products are within the range of the refining index between 1 to 5. However, from the viewpoint of restraining the clarification, the refining index should be desirably 3 or less.

The ignition temperature is in relation with the refining index, an indicator of carbonization degree and H/C. The lower the carbonization degree is (the higher the values of refining index and H/C are), the lower is the ignition point.