ELSEVIER

Journal of Hazardous Materials 58 (1998) 93–102

JOURNAL OF HAZARDOUS MATERIALS

A novel method to reuse paper sludge and co-generation ashes from paper mill

Chin-Tson Liaw *, Hui-Lan Chang, Wen-Ching Hsu, Chi-Ru Huang

Union Chemical Laboratories, Industrial Technology Research Institute, 321 Kuang Fu Road, Section 2, Hsinchu 300, Taiwan

Abstract

The purpose of this study is to develop a technology for reusing the paper sludge and co-generation ashes generated by the paper industry. The study will include the following: (1) employing granulation technology to produce a light-weight aggregate with a specific gravity less than 1.0 from paper wastes sludge, and a light-weight aggregate with a specific gravity less than 1.5 from co-generation ashes; (2) employing compounding technology to mix co-generation ashes with ceramic materials, and then to make it into constructional bricks through forming and sintering processes. The physical property tests have proved that the granulated light-weight aggregates having potential to replace the natural aggregate to make light-weight concrete. The constructional bricks made from co-generation ashes and other raw materials have a water absorption rate lower than 15%, and compressive strength greater than 150 kgf/cm^2, can conform to CNS specifications. © 1998 Elsevier Science B.V.

Keywords: Paper sludge; Co-generation ashes; Granulation technology; Sintering; Light-weight aggregate; Constructional brick

1. Introduction

The paper sludge generated from the waste water treatment units of the paper mills, with a daily volume of 3000 tons (moisture content 75%) in Taiwan, is currently one of the major waste in paper industry. Because of its large daily output and limited landfill space, although being classified as general commercial wastes, the waste has a tremendous adverse effect on the development of paper industry. Because the paper sludge

* Corresponding author. Tel.: +886 3 5732669; fax: +886 3 5732360.

PII S0304-3894(97)00123-4

consists of organic fiber material and inorganic clay material, in some foreign countries, their thermal energy is usually recovered by incineration or be converted into organic fertilizers, in some cases, recycle them into constructional materials [1–4]. Some domestic paper factories had developed the sludge incineration systems to reduce the amount of sludge and also to solve the problem of insufficient landfill sites. However, the sludge still contains 30% non-flammable materials which are collected in the form of ashes after incineration, and the amount is still considered sizable [5,6].

In view of the above facts, we employ the granulation technique to produce light-weight aggregates of different properties from paper sludge and co-generation ashes in this study. In addition, we also employ compounding and sintering techniques to make co-generation ashes into constructional bricks.

2. Materials and methods

2.1. Experimental materials

1. Paper sludge: the active sludge generated by the waste water treatment units of paper mill.
2. Co-generation ashes: the ashes generated from paper mill co-generation system.
3. Ceramics materials: clay material from brick fabrication plants.

2.2. Experimental methods

(1) Making light-weight aggregates with paper sludge.

Fig. 1 shows the flow chart of fabricating light-weight aggregates by employing the paper sludge granulation technique. The paper sludge and cement additives are weighted and then mixed extremely with mechanical running mixer. Take this mixture into pelletizing machine and start to make granules. Taking the granules into oven with 100°C ~ 105°C to remove the moisture of the granules and then the light-weight aggregate can be obtained. The physical property tests consist of water absorption rate, and volumetric specific gravity [7]. The physical properties can be obtained by the way of following step. The specimen was boiled in water for 2 h. Next, it was cooled down

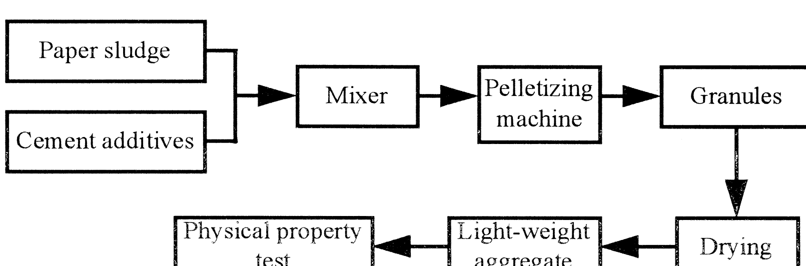

Fig. 1. Flowchart of producing light-weight aggregates from paper sludge.

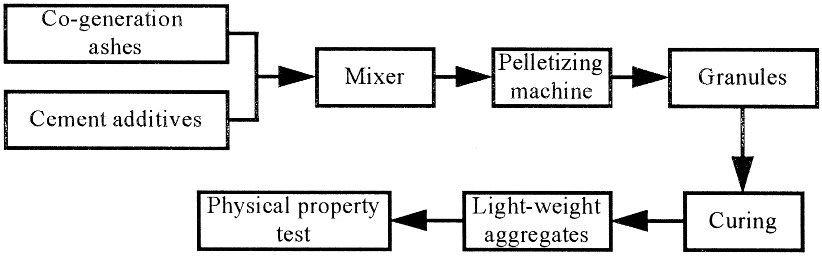

Fig. 2. Flowchart of producing light-weight aggregate from co-generation ashes.

and the water on the surface was wiped off. Specimen $(W2)$ was then weighed. Next, measured the weight (S) of the specimen hanged in water, then placed it into an oven, and dried at 105°C. Finally the weight of dried specimen $(W1)$ was measured. The formula of water absorption is:

$$\text{WA(water absorption)} = (W2 - W1) \div W1 \times 100\%$$

The formula of volumetric specific gravity is:

$$\text{VSG(volumetric specific gravity)} = W2 \div (W1 - S)$$

(2) Making light-weight aggregates with co-generation ashes.

Fig. 2 is the flow chart illustrating the experimental steps for producing light-weight aggregates from paper sludge by the granulation technique. The physical property tests include volumetric specific gravity, porosity, apparent density, water absorption rate, and single particle destructive load. The testing method and formulas of volumetric specific gravity and water absorption rate are the same to that of paper sludge light-weight aggregate, and the other testing method and formulas are stated as follows. The formula of porosity is:

$$\text{P(porosity)} = (W1 - W2) \div (W1 - S)$$

The formula of apparent density is:

$$\text{AD(apparent density)} = W2 \div (W2 - S)$$

The single particle destructive load can be obtained directly by utilizing the compressive strength testing machine.

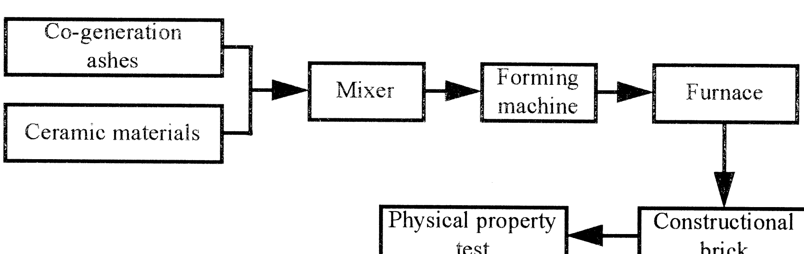

Fig. 3. Flowchart of producing construction red bricks from co-generation ashes.

(3) Making constructional bricks with co-generation ashes.

The flow chart for producing constructional bricks by forming and sintering techniques is shown in Fig. 3. The physical property tests are water absorption rate, shrinkage, density, Mohs hardness, and compressive strength.

3. Results and discussion

3.1. Materials composition analysis

Tables 1–3 shows the analysis results of chemical composition of paper sludge, co-generation ashes, and ceramics materials used in this study. The water content of

Table 1
Chemical compositions of paper sludge

	Sample 1	Sample 2	Average
Moisture content of sludge (%)	73.07	77.73	75.40
Loss of ignition of dried sludge (%)	69.96	70.26	70.11
SiO_2 (%)	38.60	37.38	37.99
Al_2O_3 (%)	51.52	51.92	51.72
Fe_2O_3 (%)	2.91	3.17	3.04
CaO (%)	4.38	5.80	5.09
MgO (%)	3.27	2.93	3.10

Table 2
Chemical compositions of co-generation ashes

Compositions	Sample	Sample 2	Sample	Average
Loss of ignition (%)	27.76	17.46	13.66	19.63
SiO_2 (%)	31.58	37.81	36.02	35.14
Al_2O_3 (%)	19.03	20.79	21.72	20.51
Fe_2O_3 (%)	3.56	3.99	3.48	3.68
CaO (%)	13.30	15.90	20.81	16.67

Table 3
Chemical compositions of ceramic materials

Compositions	Clay used for manufacturing bricks in factory A	Clay used for manufacturing bricks in factory B
Loss of ignition (%)	3.81	4.75
SiO_2 (%)	69.92	60.74
Al_2O_3 (%)	12.61	16.50
Fe_2O_3 (%)	5.36	7.29
CaO (%)	1.78	1.48
MgO (%)	1.50	2.71

paper sludge is 75.4% in average. After drying, the dried portion of sludge was then burned at 1000°C, the average weight loss amounts to 70%. In other words, the non-flammable materials in the dried sludge is only 30%, and the rest portion is flammable fibers. Table 2 shows the major chemical compositions of co-generation ashes are Al_2O_3 and SiO_2. However, CaO content is relatively higher than sludge because limestone ($CaCO_3$), which can be converted to CaO at high temperature, is added into co-generation system to absorb SO_x contained in exhaust gas. Table 3 shows the chemical compositions of the raw material used in brick fabrication plant. With SiO_2 of highest content and Al_2O_3 the second, it can form extremely hard mullite ($3Al_2O_3 \cdot 2SiO_2$) through a high temperature reaction.

3.2. TCLP (toxicity characteristic leaching procedure) test

TCLP test results of paper sludge and co-generation ashes are shown in Table 4. The extracted amounts of heavy metals are both lower than the limits required by the EPA of Taiwan, and hence fall into the category of general business wastes.

3.3. Light-weight aggregates made from paper sludge

After blending the paper sludge with different ratio of cement additives in a mixer, then spherical aggregates can be produced by a granulation machine. According to the physical analysis, we observed a trend of increasing volumetric density by increasing the weight ratio of cement and paper sludge. If the mixing time was increased from 10 min to 40 min, the aggregate volumetric density would increase considerably because the compaction of the sludge has been increased. The higher is the effect of mixing time to the volumetric density of aggregates was especially obvious when higher mixing ratio between cement and paper sludge was used.

When the mixing ratio of cement and paper sludge was 0.5, the increase of mixing time from 10 min to 40 min could bring the aggregates' volumetric density from 0.7 g/cm^3 to 1.03 g/cm^3. While the mixing time was further increased to 180 min, the

Table 4
The heavy metal concentration of TCLP leachate from paper sludge and co-generation ashes

	Paper sludge		Co-generation ashes		
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 3
Pb (mg/l)	0.41	0.69	0.44	0.48	1.34
Cd (mg/l)	0.02	0.03	0.02	0.01	0.04
Cr (mg/l)	0.11	0.21	0.03	0.05	0.18
Cu (mg/l)	0.01	0.03	0.03	0.02	0.15
Zn (mg/l)	1.62	1.48	0.05	0.03	0.22
Hg (mg/l)	ND	ND	ND	ND	ND
As (mg/l)	ND	ND	ND	ND	ND

ND indicates not detected.
Detecting limit for Hg is 0.5 $\mu g/l$, detecting limit for As is 0.1 mg/l.

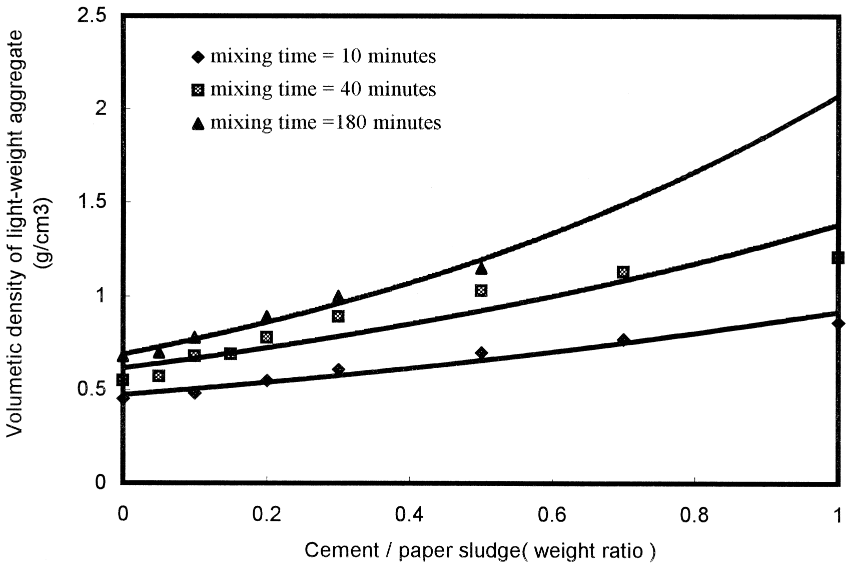

Fig. 4. Effects of cement additive quantity and mixing time on the density of light-weight aggregate.

volumetric density then increased to 1.15 g/cm^3. Evidently, the volumetric density increased considerably with a prolonged mixing time.

The purpose of this study is to develop a light-weight aggregate from paper sludge with volumetric density less than 1.0 g/cm^3. According to the experimental results, we

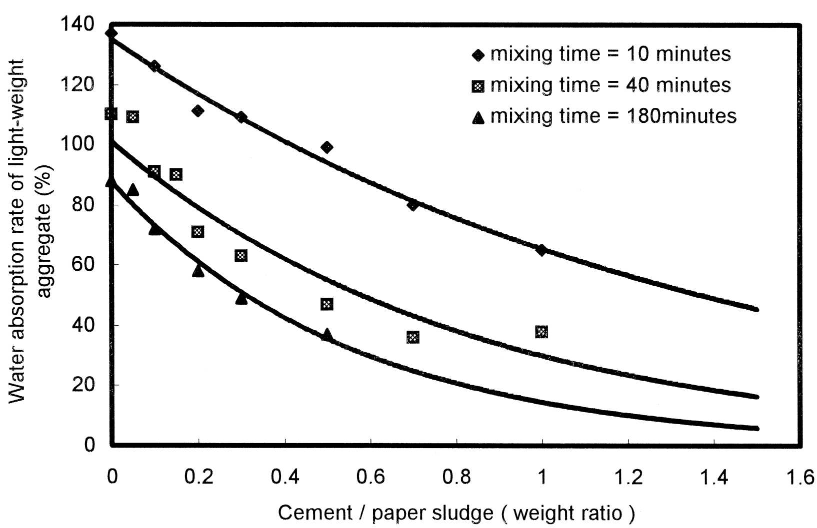

Fig. 5. Effects of cement additive quantity and mixing time on the water absorption rate of light-weight aggregate.

Table 5
Comparison between concrete bricks made from paper sludge light-weight aggregates and traditional concrete bricks made from natural gravel

Traditional concrete bricks	Light-weight aggregate concrete bricks
Size: 40 cm × 10 cm × 10 cm	Size: 40 cm × 10 cm × 10 cm
Weight: 7 kg/piece	Weight: 5.4 kg/piece
Unit volumetric weight: 1.75 g/cm^3	Unit volumetric weight: 1.35 g/cm^3

found, with a 10 min mixing time, a density less than 1.0 g/cm^3 could be reached as long as the mixing ratio of cement and paper sludge was lower than 1.1. In order to reach this goal, in case of a 40 min mixing time, the mixing ratio of cement and paper sludge must be decreased to less than 0.6. In case of a 180 min mixing time, the ratio must be less than 0.3. Those results are shown in Fig. 4.

In addition to the physical property requirement that light-weight aggregates volumetric density must be lower than 1.0 g/cm^3, the water absorption rate must also not be too high. Fig. 5 shows the analysis results of light-weight aggregates made from paper sludge. The water absorption rate decreases as the mixing ratio of cement and paper sludge increases, and also the absorption rate decreases with a prolonged mixing time. Because no clear specification concerning water absorption rate of light-weight aggregates has been formulated, we set 50% as the target in this study. We discovered from the experimental results that when the mixing time was 10 min, the mixing ratio of cement and paper sludge would have to be higher than 1.4 to meet the target of water absorption rate less than 50%. However, this would cause the aggregates to fail to meet the density requirement of less than 1.0 g/cm^3. If the mixing time was increased to 40 min, the ratio must be less than 0.6, then both targets of absorption rate of less than 50% and volumetric density of lower than 1.0 g/cm^3 could be satisfied. Likewise, with a mixing ratio of 0.3 and mixing time of 180 min, the light-weight aggregate could satisfy both the requirements of volumetric density and water absorption rate.

The light-weight concrete bricks, with a dimension of 40 cm × 10 cm × 10 cm, prepared from the granulated paper sludge weighs 5.4 kg and is about 1.6 kg lighter than conventional ones. As shown in Table 5, the unit volume weight reduces from 1.75 g/cm^3 to 1.35 g/cm^3 with as much as 23% reduction. In addition, the average

Table 6
Physical property analysis of light-weight aggregate made from co-generation ashes

	7 days of curing	28 days of curing
Porosity (%)	39.39	42.83
Water absorption rate (%)	27.56	29.16
Apparent density (g/cm^3)	2.41	2.51
Volumetric density (g/cm^3)	1.46	1.48
Single particle destructive load (kgf)	15	20

Cement additive quantity 20%, cured in atmosphere.

Table 7
Unit volumetric weight and compressive strength of light-weight concrete made from co-generation ashes when mixed with natural sand and cement

Curing (days)	Unit volumetric weight (g/cm^3)	Compressive strength (kgf/cm^2)
3	1.94	97
7	1.96	183
14	1.93	239
28	1.92	324

Concrete mixing ratio granulated aggregate:natural sand:cement = 5:3:2.

compressive strength can reach above 125 kgf/cm^2, corresponding to 1780 psi, and this is suitable for use as non-load-bearing spacing construction materials.

3.4. Light-weight aggregates made from co-generation ashes

Physical property analysis results of light-weight aggregates, conducted with an 80:20 mixing ratio of co-generation ashes and cement, after granulating and curing processes, are shown in Table 6. The granulated aggregates after 7 days curing, the destructive loads of single particles already exceeded 15 kgf. After 28 days curing, the destructive load even reached as high as 20 kgf. However, the aggregates' volumetric density was less than 1.5 g/cm^3 and lighter than the natural gravels 2.0 g/cm^3. If a concrete was made from mixing this kind lightweight aggregate, natural sand, and cement with a weight ratio of 5:3:2, after 28 days aging, the unit volume weight and compressive strength would reach 1.92 g/cm^3 and 324 kgf/cm^2, respectively. As shown in Table 7, the concrete has both light-weight and high strength characteristics.

3.5. Sintered bricks made from co-generation ashes

The major ingredients of co-generation ashes generated from paper mill are Al_2O_3 and SiO_2. They are also one of the major ingredients of ceramic materials. When an appropriate amount of ash was added into ceramics materials, after mixing, forming, and firing processes, the standard size construction bricks could be made. The physical property test results are shown in Table 8. With co-generation ash content lower than 20% and firing temperature as high as 1100°C, its quality could meet the specification of CNS for first grade of general purpose construction bricks. In other words, the water

Table 8
Characteristics of standard size construction bricks made from co-generation ashes

Co-generation ash content	Firing temperature	Water absorption rate	Shrinkage rate	Firing density	Mohs hardness	Compressive strength	Grade
10%	1100°C	5.40%	8.85%	2.23 g/cm^3	6 ~ 7	850 kgf/cm^2	Grade
20%	1100°C	11.11%	6.50%	1.87 g/cm^3	5 ~ 6	330 kgf/cm^2	Grade
20%	1080°C	18.64%	3.00%	1.80 g/cm^3	4 ~ 6	230 kgf/cm^2	Grade

absorption rate was less than 15% and compressive strength was greater than 150 kgf/cm^2. When the firing temperature was decreased to 1080°C, however, the water absorption rate of fired products would exceed 15%, and degraded to second grade while the strength also significantly decreased.

4. Conclusion

The paper sludge and co-generation ashes generated from paper mill could be reused as the raw materials of light-weight aggregate and constructional brick by employing granulation and sintering techniques. Some significant findings are summarized as follows.

(1) The major composition of paper waste sludge are organic fiber and a small amount of inorganic clay materials, and they have light-weight characteristics. After granulation process, a light-weight aggregate of volumetric density less than 1.0, particles may float on water, and a water absorption rate smaller than 50% can be obtained.

(2) The concrete bricks with a dimension of 40 cm × 10 cm × 10 cm were actually fabricated from light-weight aggregates of granulated paper sludge. Each brick weighs 5.4 kg in average and is about 1.6 kg lighter than the conventional one of 7.0 kg with as much as 23% weight reduction. Also with an average compressive strength of 125 kgf/cm^2, it can be used as non-load-bearing spacing construction materials.

(3) The high water absorption rate of light-weight aggregates made from paper sludge may be used in the future as horticulture materials to replace the imported non-water-absorbing spongy stones.

(4) The light-weight aggregates made from co-generation ashes possess the following features.

The volumetric density is below 1.5 g/cm^3

The single particle destructive strength could reach 20 kgf

The water absorption rate is below 30%

(5) Currently, no related standard for these light-weight aggregates can be followed. Table 9 shows related regulations of light-weight aggregates used in Japan. The specific

Table 9
Japanese regulations concerning light-weight aggregates

	Specific gravity for fine aggregate	Specific gravity for coarse aggregate
Japanese Industrial Standard (JIS A5002)		
Category 1	Below 1.3	Below 0.8
Category 2	1.3 ~ 2.0	0.8 ~ 1.3
Category 3	2.0 ~ 2.5	1.3 ~ 2.0
Japanese Civil Engineering Association	Below 2.0	Below 1.6
Japanese Construction Association	Below 2.0	In accordance with JIS regulations
Japanese Materials Association	Below 2.0	Below 1.8

gravity of particulated aggregates made from co-generation ashes in this study, conforms to JIS A5002 standard for the third category of light-weight coarse aggregates.

(6) Granulated aggregates made from co-generation ashes can replace the natural gravel, if mixed with natural sand and cement with a 5:3:2 weight ratio, and after 28 days curing, the compressive strength of concrete can reach 324 kgf/cm^2, and unit volume weight can reach 1.92 g/cm^3.

(7) The co-generation ashes mixed with ceramic materials by a weight ratio of 20:80, and after forming and firing at 1000°C, the quality is better than the CNS first grade general purpose bricks. In addition to better water absorption rate and compressive strength, the hardness can reach Mohs hardness 4 ~ 6 grade. Therefore, with their abrasive resistance higher than the general purpose red bricks, they may be extensively used as sidewalk pavement bricks.

References

[1] I. Ozturk, V. Erohlu, A. Basturk, Water Sci. Technol. 9 (1992) 2105–2108.
[2] V. Eroglu, A.M. Saatci, Water Sci. Technol. 2 (1993) 17–26.
[3] K. Diehn, B. Zuercher, TAPPI Journal, 1990, pp. 81–86.
[4] C.J. Hatch, R.G. Pepin, TAPPI Journal, 1985, pp. 70–73.
[5] C.T. Liaw, S.J. Hsu, C.L. Kuan, in: Proc. 4th Conf. on Industrial Waste Minimization, Taipei, 1994, pp. 233–243.
[6] H.C. Haung, in: Proc. 4th Conf. on Industrial Waste Minimization, Taipei, 1994, pp. 385–398.
[7] T.H. Pan, Experiment and Calculation of Ceramics, Hsinchu, Taiwan, 1970, pp. 14–15.