### Study on reuse of heavy metal rich sludge in ceramic pigment and construction material production

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Abstract. In this study, primarily treating waste sludge rich of Cr, Ni, Fe,...generated from electroplating wastewater treatment plant and experimentally methods of utilizing wastes as inorganic pigment in production of bricks were carried out. Economic, technical and environmental efficiency and feasibility, bases to apply to practical conditions were evaluated. The results show that water accounts for about 70% of sludge. Contents of Ni, Cr and Fe are relatively high (20, 4.5 and 2.5%, respectively). The wastes could be used to replace inorganic pigment in brick production after being primarily treated with a simple procedure. The optimal rate of replacing inorganic pigment is about 5% and 20% in case of raw material replacement. The testing results of technical parameters about compressibility, flexibility, size...show all tested products meeting with standard of brick brands commonly used in construction. Environmental safety testing based on heavy metals concentration in rain water soaking tested products (pH value

of 5.6-5.9) during 2 to 21 days shows the satisfactory in comparison to the permitted standards (TCVN 5945-2005: Fe< 5, Ni< 0.5, and  $Cr^{6+} < 0.1mg/l$ ). Cost-benefit calculations of utilizing the wastes reveal that using the wastes to replace inorganic pigment in pavement-tiled brick production gained relatively high economic efficiency and ensure the environmental safety.

Keywords: Ceramic pigment; Electroplating; Heavy metal; Sludge; Waste reuse.

### **1. Introduction**

Together with rapid development of industrialization and modernization processes, industrial waste has dramatically increased both in amount and composition. Therefore adequate behavior and proper investment for waste treatment and utilization are required. Waste sludge from electroplating system contains high content of heavy metals. Resulting from previous studies, organisms/livings could be killed or decomposed by sufficiently high concentration of heavy metal [1-3].

Currently, heavy metal rich sludge is by solidification mainly treated then disposed/land filled and incineration. In addition, some treatment methods for reuse of these wastes have been studied and obtained satisfactory results [3-7]. However, in Vietnam treatment and utilization of the heavy metal rich sludge has not sufficiently been studied and implemented. Objective of the study is to treat heavy metal rich sludge (containing chrome, nickel, and iron); reuse/utilization of treated

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sludge for replaced material as color blending (pigment) and raw material in flower brick and cement brick production.

#### 2. Experimental Method

2.1. Heavy metal rich sludge: The heavy metal rich sludge discharged from the electroplating waste water treatment system in

Goshi-ThangLong enterprise is about 1 ton of wet sludge per day.

2.2. Sludge treatment: Thickened sludge was taken and treated (see figure 1) and utilized as construction material (partly replaced raw material and color powder). Experiments were implemented in 27-7 Brick company in Thanh Son village, Kim Bang district, Ha Nam province.

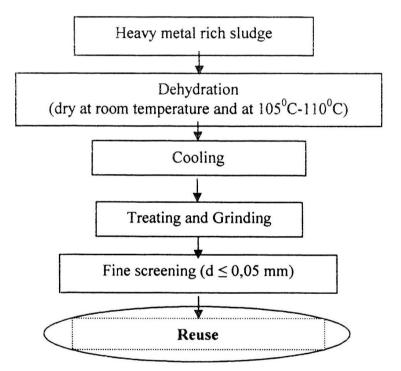


Fig. 1. Diagram of thickened sludge treatment.

2.3. Treated sludge re-usage: The experiments were carried out to reuse treated sludge as: (1) alternative partly raw material; and (2) pigment for some color and flowered bricks/enameled tiles. For the first investigation, treated sludge partly replaced raw material based on the ratio of cement and raw additive of 1: 3 (the weight of a brick is ~1.7-2.0kg). The ratio of treated sludge and raw material varied as 1:1; 1:3; 1:5; and 1:10. In the latest, treated sludge was mixed with red pigment and cement (white and black cement) a the ratio of 1:1:1.

2.4. Product test for technical parameters and environmental safety: The technical parameters including compressibility; erasability, curvature and water absorption were analyzed/tested laboratory in the of Construction material, Hanoi University of Construction. The environmental safety of sludge re-usage was assessed based on heavy metals leaching after 2, 14 and 21 days of soaking in rain water. The experiments were carried out in the laboratory of Environmental analysis, faculty of Environmental Sciences and department of Environmental analysis, Institute of Environmental Technology.

### 3. Results and discussion

## 3.1. Analysis result of heavy metal rich sludge composition

Analysis result of chemical compositions of heavy metal sludge showed that the sludge taken from Goshi -Thanh Long company contains some heavy metals like Cr, Ni, Fe with very high content, especially nickel (up to 20%). The sludge contains about 70-75% of water (table 1).

### Table 1. The main compositions of sludge

Component (%)	Sample			
-	S1	S2	<b>S</b> 3	
Nickel (Ni)	20	19.6	21,4	
Chrome (Cr)	4.15	4.54	4.32	
Iron (Fe)	2.07	2.42	2.52	
Water (H <sub>2</sub> O)	75	71	70	

Sludge samples S1; S2; S3 were taken in October, November and December 2007 In addition, the content of heavy metals and water of sludge samples taken in 3 surveys were relatively consistent.

### 3.2. Reuse of treated sludge in brick production

Treated sludge was used as partly alternative raw material and pigment of flowered bricks/enameled tiles. The replaced ratio for raw material varied as 1:1; 1:3; 1:5; and 1:10. The treated sludge was used as pigment when mixed with red pigment and cement (white and black cement) at the ratio of 1:1:1 (see table 2).

The weight of a cement brick is about 3kg of which the ratio of cement and raw material of 1:2. Cement brick produced with high ratio of treated sludge partly replaced raw material having fine surface but more sticky and more difficulty when demolishing (table 3).

Table 2. The results of the experiment in Flower brick production

Material ratio*		Altered material used for	Quality of tested products	
	1:1		Cracked surface	
Treated sludge: raw material		Main part of the bricks (sole)	Fine surface	
Treated sludge: white cement: red powder	1:1:1	Cover (surface) part	Fine pink color	

\* Number of trials is 4

Resulting from the experiments, the treated sludge and raw material ratio of 1:1 is not appropriate for both flower and cement brick production. The tested products showed that some cracked in surface or/and at the brick's edges. The lower ratio of sludge in the mixture, however, is suitable and good enough as altered material. The products have fine color and are in good quality that meet with the requirement in term of surface/cover of brick and the solidarity.

Table 3. The resu	ilts of the ex	periment in Ce	ement brick	production
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Material ratio*		Altered material used for	Quality of tested products	
	1:1		Cracked surface (in corner of bricks)	
Treated sludge: raw material	1: 3 1: 10 1: 15	Main part of the bricks (sole)	Good (fine surface)	
Treated sludge: Black cement1:1Treated sludge: White cement1:1		Cover (surface) part	Fine grey color Fine white color	

Note:\* Number of replicated experiments. In each experiment number of tested product varied from 4 to 5.

In addition, for cement bricks the mixture of sludge and white cement has brighter color in compared with black cement. However the cost should be taken into account because the price of white and black cement is approximate 120,000 and 50,000VND/m<sup>3</sup>, respectively.

The sludge and raw material ratio of 1:10 or 1:15 should produce good quality bricks. These low ratios, however, are not an effective application due to very small amount of sludge utilized whereas very large amount of sludge daily discharged. This therefore does not meet with the requirement in term of environment and waste treatment/reuse. Higher ratios (1:3 or 1:5) are strongly recommended for practice. For the ratio of 1:3, the quantity of sludge altered accounts for 18-20% total mass of the brick which is similar to the recommendation of previous studies (altered material should be less than 25% total mass) [7].

The mixture of sludge, white cement, and red powder (ratio of 1:1:1) is appropriately used as color powder for surface of flower brick. The experiment was only carried out with this ratio that referred from the previous studies [1,3].

# 3.3. Product testing for technical parameters and environmental safety

The technical assessment is based on the Vietnam standard for brick quality (TCVN 1451:1998). The testing result showed that tested products not only meet with Vietnam standard, but also is sometimes higher or better quality in comparison with origin ones.

The ratio Product	Origin brick	Sludge: raw material 1: 3	Sludge: raw material 1: 10	Sludge: raw material 1: 14	Sludge: White cement: Red powder 1:1:1
Flower brick	U 6.2	U 7.9		U 7.42	U 6.5
Cement brick (block)	M 250	M 250	M 300	M 350	

Table 4. Results in technical parameter testing of tested bricks

The quality of tested products were assessed more adequately in term of environmental and technical aspects. The results were based on the concentration of some heavy metals existing in sludge in the rain water soaked with bricks and on some technical parameters (erasable, curvature and water absorption).

As can be seen in figure 2 and 3, the concentration of Cr, Fe and Ni in rain water soaked with tested bricks is lower than Vietnamese standard TCVN 5945-2005 (0.05; 5 and 1mg/l for Cr, Fe and Ni, respectively). The higher content is obtained in the rain water soaked by higher ratio of sludge in the material mixture.

The concentration of Cr, Ni and Fe in water increased with the soaking time, particularly after 2days. From day 14 to 21 the increase seems to be slight in comparison with the beginning days.

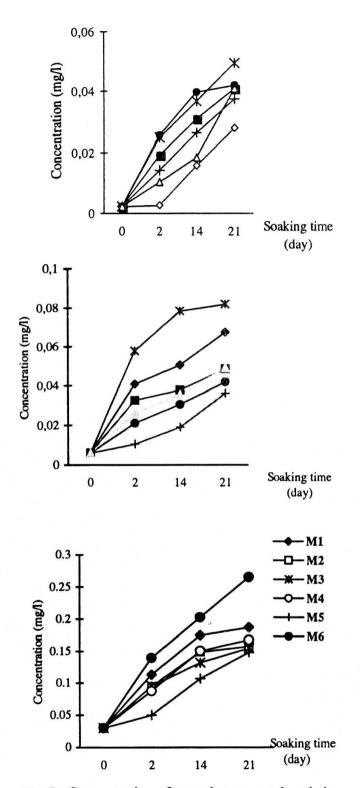


Fig. 2. Concentration of some heavy metals existing in sludge in the rain water soaking with bricks:a) Cr b) Ni c) Fe

Flower brick:

M1 – Sludge: RM=1:3 M2 – Sludge: RM=1:15 M3 – Sludge: WC:RP=1:1:1 Cement brick: M4 – Sludge: RM=1:3 M5 – Sludge: RM=1:15 M6 – Sludge: WC=1:1 The pH values of brick soaked water vary in the range of 5.6 -6.9 and slightly increase with the soaking time. The pH value of all effluents meets with the Vietnamese standard (TCVN 5945-2005, category B). The findings are in accordance with results of the other studies [3-7] (figure 3).

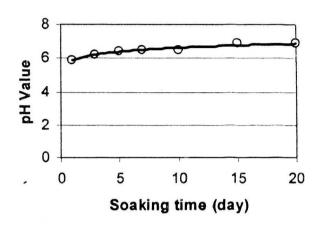


Fig. 3. The variation of pH value of rain water brick soaking.

### 3.4. Cost estimation

The results reveal that the optimal sludge replaced up to 20% of total mass for brick's sole and 5-7% for surface (as pigment) is recommended. The estimated cost and benefit analysis will be based on these ratios with the current amount of cement used (table 5).

As can be seen in the table 5, the benefit is remarkable for the solution of replace 50% of color powder by treated sludge (around 20 million VND per 100,000 bricks - monthly production rate). However for the first option (treated sludge altered raw material) lower economic benefit but more effective and valuable in waste management found because much more amount of used sludge.

Product	The ratio origin material (%)	The ratio of treated sludge (%)	Quantity of raw material and sludge*	Cost for raw material	Cost for sludge	Total cost (VND)	Benefit (balance) (VNI))
Flow	75	0	100 000 bricks x 2kg/brick x 0.75 = 150 ton	150 ton x 90 000 VND/ton = 13 500 000 VND	0	13 500000	1 500 000
Flower brick (sole replaced)	56.25	18.75	100 000 bricks x 2kg/brick x 0.5625=112.5 ton (RM) 100 000 bricks x 2kg/brick x 0.1875=37.5 ton (S)	112.5 ton x 90 000 VND/ton = 10 125 000 VND	37.5 ton x 270 000 VND/ton =1 875 000 VND	12 000000	-
Flowe	2.5	0	100 000 bricks x 2kg/brick x 0.025=5 ton	5 ton x10 000 000 VND/ton= 50 000 000 VND	0	50 000000	20 000 000
Flower brick (surface replaced)	1.25	1.25	100 000 bricks x 2kg/brick x0.0125=2.5 ton (RM) 100 000 bricks x 2 kg/brick x0.0125=2.5 ton (S)	2,5 ton x10 000 000 VND/ton =25 000 000 VND	2,5 ton x 2000000 VND/ton =5000000 VND	30 000000	-

Table 5. Estimated cost and benefit analysis for solutions of sludge reuse

Note: (\*) The input quantity required to produce 100 000 bricks/month; Average weight of a brick is 2kg. RM – Raw material; S- treated sludge

### 4. Conclusion and Recommendation

Followings are result from the study:

- The waste sludge from electroplating wastewater treatment contains very high percentages of heavy metals (Ni: 20; Cr: 4.5 and Fe 2.5%).

- After treatment, the sludge can be effectively reused as pigment for flower brick (surface), the optimal ratio of 5% is recommended and replaced raw material in flower and cement brick production with up to 20% total mass per product.

- The testing in term of environmental safety and technical parameters shows the feasibility of the utilized solution. Technical aspects meet the Construction standard when no risks for environment (heavy metal leaching into rain water) were found. In further study, heavy metal leaching into rain water with lower pH value and longer soaking time should be investigated; the use of mixing treated sludge with raw material/powder for making some other brick products (fired brick and ceramic) for optimizing product quality concerning to both environmental and technical aspects still be also the objective of the following steps.

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## Nghiên cứu tái sử dụng bùn thải giàu kim loại nặng trong sản xuất vật liệu xây dựng

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Trong công trình này đã xử lý sơ bộ bã thải rắn giàu kim loại nặng Cr, Ni, Fe...từ qui trình xử lý nước thải của dây chuyền mạ và thử nghiệm giải pháp tận dụng bã thải làm bột màu vô cơ trong sản xuất gạch lát via hè, gạch lát nền. Tính khả thi về kinh tế, kỹ thuật và môi trường cũng đã được đánh giá cụ thể để làm cơ sở triển khai áp dụng trong thực tế.

Kết quả cho thấy bã thải chứa 70% nước; hàm lượng niken, crom và sắt tương ứng 20; 4,5 và 2,5%. Bùn thải sau khi được xử lý sơ bộ với qui trình đơn giản, chi phí thấp được tận dụng thay thế một phần bột màu vô cơ cho sản xuất gạch (lát nền và gạch lát via hè). Tỉ lệ thay thế bột màu tối ưu khoảng 5%, thay thế nguyên liệu thô là 20%.

Kiểm tra các thông số kĩ thuật của sản phẩm gạch cho thấy yêu cầu về độ nén, độ uốn, độ cong vênh, kích thước... đều đáp ứng tiêu chuẩn của các Mac gạch sử dụng phổ biến trong xây dựng. Tính an toàn về môi trường được đánh giá qua nồng độ Ni, Cr, và Fe trong nước mưa sau khi ngâm sản phẩm trong 2 - 21 ngày (pH của nước mưa ngâm biến thiên trong khoảng 5,6-6,9). Kết quả cho thấy nồng độ kim loại trong nước ngâm đều dưới mức TCVN 5945-2005: Ni<0,5; Cr<sup>6+</sup><0,1 và Fe<5mg/l. Tính toán chi phí lợi ích thấy rằng giải pháp tận dụng bã thải thay thế bột màu vô cơ trong sản xuất gạch lát via hè cho hiệu quả kinh tế khá cao và đảm bảo an toàn về môi trường.

Từ khoá: Bột màu gốm; Mạ điện; Kim loại nặng; Bùn; Tái sử dụng chất thải.