

# The Potential of Heavy Metal Incorporation into Clay Precursors



N.S. Mohd Aripin, A. Abdul Kadir and A. A. Hashim

**Abstract**— High amount of heavy metal waste produced from the industrial activities has become an important global issue for several decades due to its hazardous effect on the human and environment. Since heavy metal is highly toxic and cannot be eliminated easily, the application to reuse the heavy metal waste without harming the environment must be investigated thoroughly. This paper reviews the incorporation of heavy metal into clay precursors as a good potential for the reduction of environmental pollution. The results from the previous studies show the transformation of heavy metal such as copper, zinc, lead and cadmium into less hazardous species when incorporating into clay precursors. These transformations have reduced the mobility of heavy metal as a crystalline structure is formed after the thermal treatment. It is found that the immobilization process successfully stabilizing heavy metal and increases the metal's resistance against the acidic attack through the formation of low permeable structure in the clay precursors. Hence, the incorporation of heavy metal into clay precursors is proven to be a great prospect in reducing environmental pollution.

**Keywords** : Clay Precursors, Heavy Metal, Immobilization, Leachability.

## I. INTRODUCTION

Based on data from the Department of Statistics Malaysia (2018), the population in Malaysia is estimated to be 32.4 million and predicted to grow significantly in 2020. The product demand from the increased population has also increased the industrial activities. It is undeniable that the increase of industrial activities brings positive impacts on economic growth. But, the significant concern on the detrimental effects of heavy metal to the environment has also been raised. The rapid industrial activities have produced high amount of metal waste which contributes to a large amount of land pollution due to its presence as wastewater coagulant, industrial sludge and fertilizers (Uddin 2017) [32]. Textile, mining, semiconductor and electroplating industries are also seen as the major contributors to the heavy metal

waste. Heavy metal is difficult to be eliminated or disposed to the environment due to their non-biodegradable nature. Hence, there are many studies made by the researchers in finding methods for proper management of heavy metal waste. One of the methods is to immobilize metal using sorbents or cement but this method is not reliable under acidic environment. The attempts of vitrifying toxic metal into the glass have also been carried out through a variety of thermal treatment but the result shows that the final product usage is not applicable for industrial purpose (Tang *et al.*, 2010) [29]. Recently, the building industry which uses a high amount of resources is seen as the potential sector to utilize solid waste. In order to reduce the effect of brick production to the clay utilization, the alternative to decrease its full dependency is required (Hotza & Maia, 2015) [8]. The incorporation of the heavy metal into the clay precursors through the thermal treatment process with firing temperature between 900°C to 1600°C seen to help in both the reduction of clay dependency and heavy metal pollution (Janoš *et al.*, 2010) [11].

Clay precursors are defined as the main components present in clay which are silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), ferrite (Fe<sub>2</sub>O<sub>3</sub>) and calcium oxide (CaO) (Bories *et al.* 2014) [2]. Many researchers such as He & Shih (2012), Su *et al.* (2015) and Lu *et al.* (2017) used clay precursors to represent fired clay brick in their studies as clay is the major raw material for brick. Previously, there are many successful attempts made by researcher in the incorporation of heavy metal into clay precursors. For example, copper has been successfully incorporated into alumina and ferrite by Tang *et al.* (2010), Arsenovic *et al.* (2012), Tang *et al.* (2014) and Zhang *et al.* (2018). Zinc incorporation into alumina and ferrite has also been carried out by Tang *et al.* (2012) and Hu *et al.* (2014). Since the result of these studies are encouraging, this paper further reviews the incorporation of heavy metal into clay precursors as one of the alternatives for waste management strategy. According to Velasco *et al.* (2014), the parameters involved in the incorporation of heavy metal into clay precursors possess great influence on the final product properties. Hence, the detail of the raw material, procedures, firing, drying condition and leaching test's parameters is very important. Table 1 highlights the important parameters of heavy metal utilization into clay precursors in literature. Clay precursors are defined as the main components present in clay which are silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), ferrite (Fe<sub>2</sub>O<sub>3</sub>) and calcium oxide (Cao) (Bories *et al.*, 2014) [2]. Many researchers such as He & Shih (2012), Su *et al.* (2015) and Lu *et al.*

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\* Correspondence Author

**Nur Shahirah Binti Mohd Aripin\***, Department of Science and Mathematics, Centre of Diploma Studies, University of Tun Hussein Onn, Malaysia. (Email: [shahiraharipen@gmail.com](mailto:shahiraharipen@gmail.com))

**Aeslina Binti Abdul Kadir**, Department of Water and Environmental Engineering, Faculty of Civil and Environmental Engineering, University of Tun Hussein Onn, Malaysia. (Email: [aeslina.ak@gmail.com](mailto:aeslina.ak@gmail.com))

**Azini Amiza Binti Hashim**, Department of Water and Environmental Engineering, Faculty of Civil and Environmental Engineering, University of Tun Hussein Onn, Malaysia. (Email: [aziniamizaa@gmail.com](mailto:aziniamizaa@gmail.com))

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(2017) used clay precursors to represent fired clay brick in their studies as clay is the major raw material for brick. Previously, there are many successful attempts made by researcher in the incorporation of heavy metal into clay precursors. For example, copper has been successfully incorporated into alumina and ferrite by Tang *et al.* (2010), Arsenovic *et al.* (2012), Tang *et al.* (2014) and Zhang *et al.* (2018). Zinc incorporation into alumina and ferrite has also been carried out by Tang *et al.* (2012) and Hu *et al.* (2014). Since the result of these studies are encouraging, this paper further reviews the incorporation of heavy metal into clay precursors as one of the alternatives for waste management strategy. According to Velasco *et al.* (2014), the parameters involved in the incorporation of heavy metal into clay precursors possess great influence on the final product properties. Hence, the detail of the raw material, procedures, firing, drying condition and leaching test's parameters is very important. Table 1 highlights the important parameters of heavy metal utilization into clay precursors in literature.

### II. IMMOBILIZATION OF HEAVY METAL IN CLAY PRECURSORS

Since heavy metal is hazardous, it is very important to fully understand transformation or reactions involved when heavy metal is utilized into clay precursor so that unwanted consequences for its usage can be reduced. Hence, this paper reviews the possible kinetic pathway of the heavy metal in the clay precursor. Based on Su *et al.* (2017), after the firing process, heavy metal is converted to more stable forms and immobilized in the crystal form within the clay structure. During the immobilization process, there are two simultaneous mechanisms involved which are chemical stabilization and physical encapsulation. Chemical stabilization is the process in which metal is converted into more stable and less toxic species through the thermal treatment meanwhile physical encapsulation is the process in which the stable form of metal is enclosed in the low permeability structure to prevent the escape of the metal to the environment. Two common examples of permeability structure are spinel structure and monoclinic structure. Spinel structure is found to demonstrate more stability compared to monoclinic structure (Su *et al.* 2017) [25]. The formation of spinel structure can be achieved by combining bivalent metal such as copper and zinc with trivalent metal such as aluminium or ferum (Lu & Shih 2015) [16]. The low permeable structure formed during the latter process is an important factor that could reduce the mobility of the metal during the firing process (Sena da Fonseca *et al.*, 2015) [22]. The low permeable structure provides the high alkalinity environment which allows the low solubility of heavy metal and consequently reducing the toxic metal release. Although the two processes occur simultaneously, chemical stabilization occurs at an atomic scale while physical encapsulation occurs at micron scale. During the physical encapsulation, the formation of low permeable structure prevents the leaching fluid such as acetic acid to infiltrate into them leading to their less leachable property. Many studies have proven that most of these waste form demonstrate good immobilization effect (Mymrin *et al.*, 2014; Rodríguez *et al.*, 2012) [18, 19]. Besides low permeable barrier, the

mechanical strength of metal bearing phase also has a great effect on physical encapsulation process. If the mechanical strength is low, the tendency of the waste form to break is very high and the immobilization effect will decline (Guo *et al.*, 2017) [5]. The metal immobilization in the brick can be evaluated through the leaching test. When the leachate's pH remains constant throughout the test, it shows that the metal is fully immobilized and form crystalline structure in which the leachate could not pass through.

### III. LEACHABILITY OF HEAVY METAL IN CLAY PRECURSORS & RESULTS

Heavy metal leaching happens when heavy metal which originally bound in minerals start to mobilize and converted into metal ions when releasing into the aqueous solution. Leaching test is very crucial to identify the effectiveness of metal immobilization in clay precursors after the thermal treatment (Tang *et al.*, 2014) [27]. This is to ensure that the utilization of heavy metal into clay precursors complies with the environmental standard (Leiva *et al.*, 2016) [12]. There are varieties of leaching method to be chosen depending on the particular use of leaching test and targeted components in the test. The most common leaching methods are European Methods, US EPA methods and ASTM Standard Methods. There a few tests available under European Methods such as tank leaching test (NEN 7345), availability test (NEN 7341) and column test (NEN 7343). Salim *et al.* (2018) and Cusidó & Cremades (2012) uses NEN 7345 standard to study the leaching behavior of heavy metal such as As, Ba, Cd, Ni, Cu, Pb, Zn, V, Ba and Cr when these metals are incorporated into fired clay brick. However, as far as it is concern, there are no researchers that used this leaching method to test metal immobilization in the clay precursors. Most of them are using Toxicity Characteristic Leaching Procedure (TCLP) which is listed under US EPA leaching method. For example, Lu and Shih (2011), Hu *et al.* (2014), Tang *et al.* (2014) and Mao *et al.* (2014) used TCLP in evaluating leaching of heavy metal such as Pb, Zn and Cu from alumina, ferrite and silica. There are many methods listed in ASTM Standard Methods such as ASTM Method D-3987, ASTM Method D-4793, ASTM Method D-5233 and ASTM-D5284. According to Singh *et al.* (2018), ASTM Method D-3987 is a frequent method used to generate leachate from fly ash or coal ash to estimate the mobility of metal such as Mg, Cr, Zn, Pb, Mo and Mn. Plus, there are also researchers who use Constant-pH leaching test (CPLT) in evaluating Pb and Cd leaching (Lu & Shih 2015; Lu *et al.*, 2017; Su *et al.*, 2019) [16, 14, 26]. Apart from these four methods, there are other researchers such as Li *et al.* (2017) and Zhang *et al.* (2018) who use leaching toxicity-acetic acid buffer solution method to leach Cu, Pb, Cd and Zn. The next sub-section reviews the leachability of the common heavy metal utilized in the clay precursor.

#### A Copper

There are some studies which have been exploring the possibility of copper incorporation into clay precursors. For example, Tang *et al.* (2014) successfully incorporating copper into transition aluminas;  $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ .

When sintering copper with  $\gamma\text{-Al}_2\text{O}_3$  at  $750^\circ\text{C}$ , the formation of  $\text{CuAl}_2\text{O}_4$  was observed. The  $\text{CaCuO}_3$  was also formed at this temperature but in the small amount. After increasing the temperature to  $1100^\circ\text{C}$ , the  $\text{CuO}$  reactant reappeared with the production of  $\text{CuAlO}_2$ . As for  $\alpha\text{-Al}_2\text{O}_3$  system, all the products formed are similar but  $\text{CuAl}_2\text{O}_4$  was formed in a smaller amount at higher temperature of  $850^\circ\text{C}$  compared to  $\gamma\text{-Al}_2\text{O}_3$  system. This shows that copper stabilizing into  $\gamma\text{-Al}_2\text{O}_3$  is more favorable compared to  $\alpha\text{-Al}_2\text{O}_3$  at lower temperature. Then, the leachability of copper from the reactant and all products are evaluated through prolonged TCLP using acetic acid with pH of 2.9. After 20 days,  $\text{CuO}$  reactant was found to increase the pH to the highest value between 4.6 to 4.8 with  $1500\text{ mgL}^{-1}$  of leached copper while  $\text{CuAl}_2\text{O}_4$  shows the lowest pH value which remains very close to the initial pH with only  $190\text{ mgL}^{-1}$  of leached copper, consistent with the result reported by Tang et al. (2010) and Tang & Shih (2013). Another study conducted by Hu et al. (2010) using prolonged TCLP with the usage of hydrochloric acid as the leaching fluid also demonstrated almost similar result. They revealed that the high amount of leached copper from  $\text{CuO}$  and  $\text{Cu}_2\text{O}$  is due to dissolution of crystal cations that exchanged the protons with the ion in the hydrochloric acid which then allow the acid to damage the crystal. When the crystal is damaged, the copper is released to the leaching fluid and lead to the pH increase. The results from all the aforementioned studies clearly show that the sintering of multi-phase copper-bearing sludge into alumina clay precursor is a reliable technique to prevent the leaching of copper to the environment.

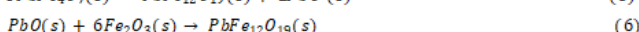
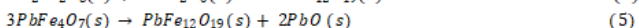
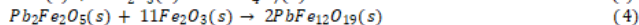
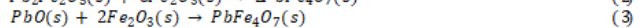
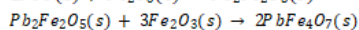
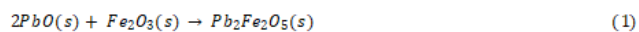
### B Zinc

Through the controlled scheme of thermal treatment, zinc metal can also be stabilized by clay precursors. It has proven that the spinel-type crystalline structure formed through the thermal reaction of these zinc metal and alumina-rich material causes a substantial reduction in the zinc leachability under acidic condition (Tang et al., 2011; Arsenovic et al., 2012; Hu et al., 2014) [31, 1, 10]. When firing the mixture of zinc metal and two alumina precursors from  $750^\circ\text{C}$  to  $1450^\circ\text{C}$  for 3 hours,  $\text{ZnAl}_2\text{O}_4$  is observed as the most stable zinc phase at a sintering temperature of  $1450^\circ\text{C}$  and  $1250^\circ\text{C}$  for  $\gamma\text{-Al}_2\text{O}_3$  and  $\alpha\text{-Al}_2\text{O}_3$ , respectively. Even though the leaching test was carried out for 22 days, the  $\text{ZnAl}_2\text{O}_4$  leachate pH remains constant until the end of the experiment compared to  $\text{ZnO}$  leachate pH which increases rapidly in just 18 hours.  $\text{ZnO}$  leachate pH is found to be three order of magnitude higher than.  $\text{ZnAl}_2\text{O}_4$ . It shows that  $\text{ZnAl}_2\text{O}_4$  has the strongest resistance towards acidic attack while  $\text{ZnO}$  is only vulnerable to proton-mediated dissolution. Plus, to reflect the reliability of zinc utilization in clay precursors, the leaching of sludge containing zinc metal from electroplating industry mixed with alumina, ferrite and silica was tested. The leachability of sample was tested to both whole sample and ground sample powder. It is found that the concentration of zinc in leachate is higher for the sample powder compared to the normal sample due to the higher exposed surface area. This shows that heavy metal stabilization can also be affected by the chemical mineral transformation. Nevertheless, the concentrations of zinc leached for both of the sample still

comply with the standard regulation. Thus, it can be deduced that even though the fired clay brick produced with the incorporation of heavy metal into clay precursors are abandoned for a long time, it can still be classified as non-hazardous material compared to the metal's direct disposal to the environment. Based on the most recent study about zinc incorporation conducted by Tang et al. (2016), they compared the possible incorporation of zinc into  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{SiO}_2$  with the firing temperature between  $650^\circ\text{C}$  to  $1450^\circ\text{C}$ . In  $\gamma\text{-Al}_2\text{O}_3$  system,  $\text{ZnO}$  is completely transformed into  $\text{ZnAl}_2\text{O}_4$  at temperature of  $1050^\circ\text{C}$  while  $\text{ZnO}$  is completely transformed into  $\text{Zn}_2\text{SiO}_4$  at higher temperature of  $1350^\circ\text{C}$  in  $\text{SiO}_2$  system. It shows that the stabilization of zinc can be achieved at lower temperature in  $\gamma\text{-Al}_2\text{O}_3$  system compared to  $\text{SiO}_2$  system. The amount of leached zinc for  $\text{ZnAl}_2\text{O}_4$  after 18 hours of TCLP is also very low with only  $2\text{ mgL}^{-1}$ .

### C Lead

Several researchers have been working on stabilizing lead in the clay precursors. For instance, Lu & Shih (2011) observe the lead stabilization mechanism in alumina. Lead oxide is used to represent lead metal as most metals are oxidized at high temperature. When the sintering temperature reaches  $700^\circ\text{C}$  and  $950^\circ\text{C}$ ,  $\text{PbAl}_2\text{O}_4$  and  $\text{Pb}_9\text{Al}_{12}\text{O}_{19}$  product was formed. These two potential hosting phases for lead are then further analyzed using prolonged TCLP of 7 days under acidic condition. After the leaching test, it is found that the pH of leaching fluid increases for  $\text{PbAl}_2\text{O}_4$  phase while the pH remains constant at initial value for  $\text{Pb}_9\text{Al}_{12}\text{O}_{19}$ . The increase of leaching fluid pH is due to the ion exchange process happened between the crystal cations and protons ion in the solution which leading to the complete destruction of the crystal structure. The constant pH of leaching fluid shows that only  $\text{Pb}_9\text{Al}_{12}\text{O}_{19}$  phase is stable under acidic condition. Besides, it is also demonstrated at the end of this study that the lead oxide form is incapable of stabilizing lead under acidic attack. The finding of this study similar to Lu and Shih (2015). Although transition alumina is used as clay precursor,  $\text{Pb}_9\text{Al}_{12}\text{O}_{19}$  is still proven to have the strongest resistance to acidic leachate. Lu et al. (2017) also investigated the transformation of lead in ferrite at sintering temperature between  $600$  to  $1000^\circ\text{C}$ . At a low temperature of  $700^\circ\text{C}$ , the formation of  $\text{Pb}_2\text{Fe}_2\text{O}_5$  was observed. After increasing the sintering temperature to  $750^\circ\text{C}$ , another two lead bearing phases which are  $\text{PbFe}_4\text{O}_7$  and  $\text{Pb}_9\text{Al}_{12}\text{O}_{19}$  were formed. The formation of the three compounds can be deduced as follow:



After 7 days, the total concentration of lead in the leaching fluid was analyzed by inductive coupled plasma-atomic emission spectroscopy (ICP-AES). The result of Constant-pH Leaching Test (CPLT) reflected that the most preferable lead bearing phase is  $\text{Pb}_2\text{Fe}_{12}\text{O}_{19}$  as it has total resistance towards acidic condition.

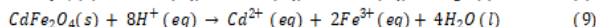
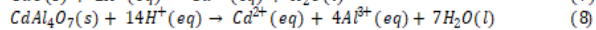
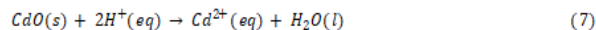


This is because there are structural defects detected in  $Pb_2Fe_2O_5$  and  $PbFe_4O_7$ . In  $Pb_2Fe_2O_5$ , the presence of defect on the layer of atomic arrangement has facilitated the opportunity for larger amount of lead to be leached from its structure. As for  $PbFe_4O_7$ , even though it has the almost similar structure to  $Pb_2Fe_{12}O_{19}$ , the vacancy of lead oxide in its atomic arrangement has increased the probability of lead to escape from its crystal structure.

D Cadmium

Amongst all metals, cadmium has the most mobility in water as it is highly soluble in water. To make it worse, cadmium oxide which was formed at slightly high temperature shows great mobility in the acidic environment. This means when cadmium oxide is in contact with acid, the cadmium will be leached out and become a huge threat to the environment. Thus, there are a few works investigating on stabilizing sludge containing cadmium using clay precursors. Su *et al.* (2015) and Su *et al.* (2017) have been successfully incorporating cadmium into  $\gamma-Al_2O_3$  and  $\alpha-Fe_2O_3$  structure.  $CdAl_4O_7$  with monoclinic structure is found to be the most stable cadmium bearing phase in  $\gamma-Al_2O_3$ . The optimal temperature and Cd/Al ratio for its formation are 950°C and 0.25. Meanwhile, for  $\alpha-Fe_2O_3$  structure,  $CdFe_2O_4$  with spinel structure shows the most stability at a temperature of 850°C

and 0.5 Cd/Fe ratio. This shows that  $\alpha-Fe_2O_3$  system shows more encouraging result for cadmium stabilization since the bearing phase produced has more stable structure and has higher cadmium incorporation efficiency at lower temperature when compared to  $\gamma-Al_2O_3$  system. In order to evaluate the effectiveness of the thermal treatment, the cadmium bearing phase was tested by CPLT using nitric acid (pH=4.0) as leaching fluid and the result was compared to the CdO reactant. The equations below show the congruent dissolution of CdO,  $CdAl_2O_4$  and  $CdFe_2O_4$  in nitric acid.



From the leaching test, it is found that the leached amount of cadmium for all the tested samples gradually increased over time. Throughout the leaching period, it is demonstrated that the amount of cadmium leached from  $CdAl_4O_7$  was two order lesser than cadmium oxide meanwhile for  $CdFe_2O_4$ , its cadmium leached significantly lesser than CdO by three order of magnitude. From the result, it can be concluded that the transformation of the metal phase to crystal structure can improve the inherent robustness of cadmium-hosting products to acid (Sanjabi & Obeydavi 2015) [21].

Table I Important Parameters of Heavy Metal Utilization into Clay Precursors

Researcher	Clay Precursor	Heavy metal	Mixing ratio	Mixing time (h)	Size of sample	Molding method	Drying condition	Firing condition	Leaching test		
									Type	Leaching fluid & pH	Leaching period (h)
Tang et al. (2010) [29]	$\gamma-Al_2O_3$	Synthetic CuO	0.5	18	20-mm pellet	Pressing (650 MPa)	Room temp.	650 - 1150°C for 3h	Prolonged TCLP	Acetic acid pH 2.9	528
Hu et al. (2010) [9]	$\gamma-Al_2O_3$	Synthetic CuO	0.5	24	16-mm pellet	Pressing (6 MPa)	105°C for 48h	600 - 1200°C for 3h	Prolonged TCLP	HCl acid pH N/A	264
Tang et al. (2011) [31]	$\alpha-Al_2O_3$ $\gamma-Al_2O_3$	Synthetic ZnO	0.5	18	20-mm pellet	Pressing (650 MPa)	Room temp.	750 - 1450°C for 3h	Prolonged TCLP	Acetic acid pH 2.9	528
Lu & Shih (2011) [15]	$Al_2O_3$	Synthetic PbO	0.083 - 0.5	18	20-mm pellet	Pressing (650 MPa)	Room temp.	600 - 1000°C for 3h	Prolonged TCLP	Acetic acid pH 2.9	576
Arsenovic et al. (2012) [1]	$Fe_2O_3$ $Al_2O_3$	Pb, As, Cr, Zn, Cu, Ni and Ba from galvanizing industry	0.03 & 0.06	N/A	120 x 50 x 14 mm, 55.3 x 36 x 36 mm, 30 x 30 x 30 mm	Using laboratory extruder	105 ± 5 °C	870 - 1020°C	N/A	Water pH N/A	N/A
He & Shih (2012) [7]	$\gamma-Al_2O_3$	Synthetic NiO	0.5	22	13-mm pellet	Pressing (125 MPa)	95°C	1140 - 1480°C for 3h	N/A	Nitric acid pH N/A	2.67

Tang & Shih (2013) [28]	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Synthetic CuO	0.5	18	20-mm pellet	Pressing (650 MPa)	N/A	650 - 1150°C for 3h	Prolonged TCLP	Acetic acid pH 2.9	528
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Wang et al. (2012) [34]	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Synthetic NiO	0.5	22	20-mm pellet	Pressing (650 MPa)	95°C for 72h	750 - 1250°C for 3h	N/A	N/A	N/A
Tang et al. (2014) [27]	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Cu from sludge treatment facility	0.3	18	20-mm pellet	Pressing (480 MPa)	105°C	750 - 1250°C for 3h	Prolonged TCLP	Acetic acid pH 2.9	480

Researcher	Clay Precursor	Heavy metal	Mixing ratio	Mixing time (h)	Size of sample	Molding method	Drying condition	Firing condition	Leaching test		
									Type	Leaching fluid & pH	Leaching period (h)
Mao et al. (2014) [17]	Fe <sub>2</sub> O <sub>3</sub>	Synthetic PbO	0.083	18	Cylindrical pellet 13-mm diameter	Pressing (10 MPa)	105°C for 24h	650 - 1400°C for 3h	Prolonged TCLP	Acetic acid pH 2.9	528
Hassan et al. (2014) [6]	N/A	Ar and Fe from arsenic-iron removal plant	0.03 - 0.12	N/A	250 x 125 x 75 mm	Hand molding into wooden frames	105°C for 48h then 500°C for 12h	900 - 1000°C for 12h	N/A	Fluid N/A pH 3, 6.5, 12	216
Hu et al. (2014) [10]	SiO <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>3</sub>	Zn and Pb from zinc smelting slag	0.6	N/A	Cylindrical pellet 20-mm diameter, 40 mm height	Pressing (5 MPa)	105°C	900 - 1100°C for 4h	TCLP	Sulphuric-nitric acid pH 3.2	18
Lu & Shih (2015) [16]	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Synthetic PbO	0.083 - 0.5	18	20-mm pellet	Pressing (650 MPa)	Room temp.	600 - 1000°C for 0.25h - 10h	CPLT	Acetic acid pH 4.9	92
Su et al. (2015) [24]	$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Synthetic CdO	0.25 & 0.5	18	20-mm pellet	Pressing (250 MPa)	105°C for 24h	800 to 1000°C for 3h	CPLT	Nitric acid pH 4.0	2
Tang et al. (2016) [30]	SiO <sub>2</sub> $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Synthetic ZnO	0.5	18	20-mm pellet	Pressing (250 MPa)	N/A	650 - 1450°C for 3h	Prolonged TCLP	Acetic acid pH 2.9	528
Su et al. (2017) [25]	$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Synthetic CdO	0.25 & 0.5	N/A	20-mm pellet	Pressing (250 MPa)	105°C for 24h	600 to 1000°C for 3h	CPLT	Nitric acid pH 4.0	2
Lu et al. (2017) [14]	Fe <sub>2</sub> O <sub>3</sub>	Synthetic PbO	0.083 - 0.25	18	20-mm pellet	Pressing (650 MPa)	Room temp.	600 - 1000°C for 3h	CPLT	Fluid N/A pH 4.9	168

Zhang et al. (2018) [35]	SiO <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>3</sub>	Cr, Zn, Cu and Ni from electroplating industry	0.02 – 0.10	0.5	50 x 35 x 10 mm	Using laboratory pressure machine (40 MPa)	110°C for 24h	50 – 950°C for 3h	Leaching Toxicity-acetic Acid Buffer Solution Method	Acetic acid pH 2.9	480
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#### IV. CONCLUSION

In conclusion, it is proven that the incorporation of heavy metal into clay precursors possesses great potential as an alternative to metal waste management besides reducing the full dependency on clay to produce fired clay brick. This method enables the stabilization of metal under acidic condition. However, while much success has been achieved at the laboratory scale, these efforts have not gained commercial popularity due to the lack of attention on optimum process parameters that must be used in industrial process. When the process parameters such as mixing ratio or the firing temperature is not carefully studied and chosen, the incomplete combustion in brick's firing tends to occur and consequently lead to the production of unwanted substances which will pollute the environment. Hence, more extensive studies on the design for the scaling up of the heavy metal incorporation into clay precursors should be conducted to reflect the promising results for the industrial application.

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## AUTHORS PROFILE



**Nur Shahirah Binti Mohd Aripin.** Lecturer at Department of Science and Mathematics, Centre of Diploma Studies. Previously, she completed Master in Chemical Engineering at Universiti Kebangsaan Malaysia. She has journal and book publications in Science and Technology.



**Aeslina Binti Abdul Kadir.** Associate Professor and Deputy Dean of Student Affairs and Alumni at Faculty of Civil and Environmental Engineering Universiti Tun Hussein Onn Malaysia with 16 years of teaching experience. She has various projects and publications in solid waste management, waste recycling and sustainable building material.



**Azini Amiza Binti Hashim** Master by Research student in Civil Engineering, Universiti Tun Hussein Onn Malaysia. Previously, she completed her Bachelor Degree in Engineering (Chemical) at Universiti Teknologi Malaysia.