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# Solidification/stabilization Treatment of Spent Catalyst ($V_2O_5$) from a Sulfuric Acid Plant using Ordinary Portland Cement (OPC) and an Additive

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**Abstract** Vanadium pentoxide ($V_2O_5$) is the most commonly used oxidation catalyst in the production of sulfuric acid. It has a service life of 5 - 10 years and is disposed after its deterioration. Spent catalyst is listed as a scheduled waste under Malaysian Environmental Quality Act (EQA), 1974 and it must be sent to Kualiti Alam Sdn. Bhd. (KA), the only integrated hazardous waste treatment and disposal centre in peninsular Malaysia. Since 2005, an amended regulation allows the spent catalyst to be treated by the waste generator, provided a positive scientific outcome is presented. This paper discusses a scientific study of the spent catalyst treatment using the cement-based solidification/stabilization (S/S) technique, whereby the treatment effectiveness was investigated through two leaching tests, TCLP and ANS 16.1 (modified). The spent catalyst is a dry, greenish-yellow porous cylindrical solid, which contains mainly silica (56 - 75%). Its metal contents are K (839mg/l), V (356mg/l), Na (99mg/l), Al (44mg/l), Ca (23mg/l), Fe (13mg/l), Mg (13mg/l) and Pb (0.7mg/l). Cement-based S/S was able to control the leaching of the Fe and Pb that exceeded Malaysian EQA wastewater standard limit before the treatment. In addition, leachability index ($L_i$) confirmed that the waste constituents were successfully encapsulated in the solidified matrix. The compressibility of the treated samples was measured using ASTM unconfined compressive strength and proved that they should be able to sustain the load placed on them in a landfill. Tiles and bricks made from the S/S process could potentially be used as construction materials.

**Abstrak** Vanadium pentoxide ($V_2O_5$) adalah “catalyst” yang paling kerap digunakan di dalam penghasilan asid sulfirik. Ia mempunyai tempoh berguna sepanjang 5 – 10 tahun dan akan dibuang apabila mula mengurai. Sisa “catalyst” adalah disenaraikan sebagai “scheduled waste” dibawah akta Kualiti Alam Malaysia (1974) dan harus dihantar ke Kualiti Alam Sdn. Bhd. (KA) iaitu satu-satunya pusat rawatan dan penghapusan sisa yang terintegrasi di Malaysia. Sejak 2005, perubahan pada rang undang-undang membolehkan sisa “catalyst” untuk dirawat oleh penghasil sisa sendiri, tertakluk kepada bukti saintifik mengenai rawatan yang berkesan dapat diperolehi. Kertas saintifik ini membincangkan rawatan sisa “catalyst” menggunakan teknik “solidification/stabilization” (S/S) berasaskan simen. Kecekapan rawatan ini diselidiki melalui two ujian “leaching” iaitu TCLP and ANS 16.1 yang diubahsuai. Sisa “catalyst” adalah berbentuk silinder yang kering dan berwarna hijau-kuning dan terdiri daripada silica (56 - 75%). Dari segi logam, ia terdiri daripada K (839mg/l), V (356mg/l), Na (99mg/l), Al (44mg/l), Ca (23mg/l), Fe (13mg/l), Mg (13mg/l) dan Pb (0.7mg/l). Rawatan S/S berasaskan simen didapati berupaya mengurangkan kadar “leaching” yang melebihi tahap yang dibenarkan oleh akta Kualiti Alam Malaysia sebelum rawatan dilakukan. Tambahan pula, indeks kebolehan “leaching” mengesahkan komponen sisa “catalyst” telah terkurung didalam matriks simen. Kemampatan sampel yang dirawat diukur menggunakan kaedah “ASTM unconfined compressive strength” dan sampel yang dirawat dapat menahan beban yang boleh dikenakan keatasnya di dalam kawasan pelupusan sampah. Kepingan lantai dan bata yang dihasilkan daripada proses S/S boleh juga digunakan sebagai bahan binaan.

(Scheduled waste, cement-based solidification/stabilization, TCLP, ANS 16.1, compressive strength)

## INTRODUCTION

Malaysian industries generated more than 300,000 metric tons of hazardous waste (scheduled waste) annually for the past 7 years. In 2004, 58% of scheduled wastes were delivered to local off-site recovery facilities, 19% were treated and disposed at the integrated Kualiti Alam Treatment Disposal Facility, 11% were sent to other onsite treatment (land farms and incinerators), 8% sent for off-site storage, 3% incinerated at clinical waste incinerator and 0.7% exported for recycling [1].

Spent catalyst used in the oxidation of gaseous $SO_2$ to $SO_3$ in sulfuric acid production contains a high amount of diatomaceous earth silica and crystalline silica [2]. These materials are in porous cylindrical pellet form and used as a carrier for the oxidation agent, vanadium pentoxide ($V_2O_5$). Besides, there are other alkali-metal promoters ($K_2SO_4$ and $Na_2SO_4$) that are mixed with $V_2O_5$ in order to increase the activity of the catalyst. Chemical safety data sheet states that the spent catalyst contains quartz that may cause lung cancer [3]. According to Williamson *et al.* [4], inhalation of quartz dust is linked with decreased lung function although the mechanisms involved are poorly understood. Inhalation of vanadium fume (as $V_2O_5$) will have adverse health effects on the respiratory systems, skin and eyes and it is listed as a carcinogen in the European Union [5].

Spent catalyst is listed as a scheduled waste under Malaysian Environmental Quality Act 1974, Environmental Quality (Scheduled wastes) Regulation 2005. According to this regulation, all scheduled wastes generated must be recorded, stored, labeled (by the waste generator), treated and disposed of at the prescribed premises. The treatment cost will be borne by waste generators, and this is burdensome for Small and Medium Industries (SMI). Nevertheless, revised regulations give an option for the waste generator to avoid the cost. It states that a waste generator could apply to have the scheduled wastes excluded from being disposed of, treated or recovered at the prescribed premises if it could be proved that the waste is not toxic and hazardous. For this, the hazardous characteristics such as corrosivity, ignitability, reactivity and toxicity should be removed. This could be achieved by S/S and this is one of the objectives of this work.

Solidification/stabilization (S/S) is an established technology in the treatment of hazardous waste [6]. It was originally used in the treatment of low-level radioactive waste [7]. In S/S treatment, the hazardous waste is chemically transformed into a stable and less mobile form so that the waste elements will be entrapped in the solidified matrix. A few types of binders are commonly used in the S/S treatment method such as cement (OPC), pozzolan, thermo-plastic and organic polymers, etc. The selection of the binder will depend on the compatibility of the binder with the characteristics of the waste.

Cement-based S/S is quite suitable in treating waste that contains inorganic constituents. It has a strong acid neutralization capacity (ANC), which is very important in treating the acidic nature of inorganic waste and is low in economic costs [8]. According to LaGrega *et al.* [9], lack of a better alternative and availability of a physiochemical mechanism (such as cement-based precipitation and absorption at high pH) contribute to the advantages of cement-based stabilization.

The objectives of this study are to determine the effectiveness of S/S treatment on spent catalyst generated from a sulfuric acid plant, and the suitability of the S/S treated waste to be disposed of safely in a secure landfill. The Toxicity Characteristics Leaching Procedure (TCLP) was adopted in 1986 by the USEPA under the Hazardous and Solid Waste Amendments of 1984 [10]. It is used to determine whether a treated waste meets the applicable standards. American Nuclear Society Leach Test (ANS 16.1), on the other hand, is used to calculate the rate of loss of waste constituents. Current Malaysian regulations are being amended so that the S/S products such as tiles and bricks could be used as construction materials.

## METHODOLOGY

### Material

The spent catalyst was collected from a sulfuric acid production company. Ordinary Portland Cement (OPC) was used as the binder and sodium silicate solution was used as an additive to enhance the treatment. OPC is an excellent material because it is cheap, plentiful, and reasonably tolerant of chemical variations [11] and it is suitable in treating waste containing inorganic materials [12]. A combination of liquid soluble silicates and cement form the basis of a process that has been demonstrated to be effective in stabilizing soils contaminated with high concentration of lead, copper, and zinc [10].

### Characterization of physical and chemical properties of spent catalyst

The spent catalyst was analysed for its moisture content, density, pH and metal content. For moisture content, ASTM Test Methods D-2216 was used. The specific gravity of the solid was measured using the method described by Miroslav and Vladimir [13]. The pH of the spent catalyst at a solid: distilled water (g/ml) ratio of 1:2 was measured using a Hanna Instrument Membrane pH meter. USEPA 3050B Acid Digestion Method was used to determine the elemental content of the samples to establish the type and quantity of metals to be stabilized via the S/S method.

### Solidification/Stabilization

#### i. Sample preparation

Cylindrical solidified matrices (height-to-diameter ratio of 0.3) were prepared by mixing binder materials with spent catalyst. Ordinary Portland Cement (OPC) was used as a binder and sodium silicate solution (SS) was used as an additive. Spent catalyst (SC) was crushed to fine particles with size smaller than 1mm, as per standard protocol for efficient binding. OPC, SC and SS were added according to the prefixed ratio, on dry weight basis (Table 1). Two sets of samples were prepared for both TCLP and ANS 16.1 (modified) leaching tests. For ANS 16.1 leaching test matrix, a nylon fishing line, to avoid any metal contamination, was attached in the middle of each matrix.

The constituents were homogenized using a blender for 3 minutes. Water was added slowly into the dry mix (pre-determined water: cement ratio of 0.48 to 1.0) to promote hydration. The mixture was then mixed at high speed for 3 - 4 minutes. The resulting waste-loaded grout paste was transferred to paper cups that were used as moulds. The paper cups were covered with Lucite sheets and left undisturbed for 24 hours at room temperature 27 - 34°C and a relative humidity of 92%. The matrices were removed from the paper cups and further cured for 27 days under dry condition to simulate the drying condition as normally practiced before landfilling.

**Table 1.** Combination of OPC, SS and SC

| ORDINARY PORTLAND CEMENT (% WEIGHT) | SODIUM SILICATE SOLUTION (% WEIGHT) | SC (% WEIGHT) |
|---|---|---|
| 30 | - | 70 |
| 40 | - | 60 |
| 50 | - | 50 |
| 60 | - | 40 |
| 70 | - | 30 |
| 23 | 7 | 70 |
| 34 | 6 | 60 |
| 45 | 5 | 50 |
| 56 | 4 | 40 |
| 67 | 3 | 30 |

#### ii. Leach tests

#### Toxicity Characteristic Leaching Procedure (TCLP) – Leach Protocol

The TCLP protocol (U.S EPA method 1311) was performed using the solidified samples that were crushed to particle size smaller than 9.5mm and transferred to flasks. Acetic acid solution adjusted to pH 2.88 ± 0.05 was established as the appropriate extraction fluid. A liquid-to-solid ratio of 20:1 was used. The flasks were then covered with parafilm, capped with aluminium foil, and then mechanically shaken for 18 hours continuously at 300rpm as per protocol, at a temperature of 25°C.

After 18 hours contact time, leachate was filtered through at 0.8-μm pore size borosilicate glass fiber filter to separate the solid and liquid phases. The filtrate, i.e., the TCLP extract, was measured for pH. Heavy metals in the TCLP extract were analyzed using Inductively Coupled Plasma-Emission Spectroscopy (ICP-AES, Baird Model 2000).

### American Nuclear Society (ANSI/ANS 16.1) (modified)

Cylindrical solidified matrices (thickness-to-diameter ratio of 0.3) were suspended using nylon fishing lines into the leachant (ultra pure water of resistivity >18 MΩ-cm, processed by ELGASTAT® UHQPS). The ratio of leachant volume ($cm^3$) to external geometric surface area ($cm^2$) of the solid matrices is 10 $\pm$ 0.2 (cm) [14]. The leachant was contained in plastic containers made of non-reactive polypropylene. The matrices were suspended for a maximum period of 28 days. Leachate samples were collected on the first, third; seventh, fourteenth and twenty-eighth day and fresh leachants were replaced. The pH of each leachate sample was measured. The leachate samples (10ml) were collected, acidified with 1 ml nitric acid and stored in refrigerator before it was analyzed using ICP-AES.

Leaching rate, $l$ (cm/day), as a function of the leaching time was calculated using equation (1) [14]:

$$l = \left(\frac{a_n}{A_o}\right)\left(\frac{V}{S}\right)\left(\frac{1}{t_n}\right) \qquad (1)$$

where $a_n$ is the amount of the constituent of interest leached during interval n (mg/L), $A_o$ is the amount of the constituent of interest initially present in the matrix (mg/L), V/S is the ratio of matrix volume to surface area ($cm^3/cm^2$) and $t_n$ is the leaching time since the beginning of the first leaching interval (s).

Leachability Index, *Li* (dimensionless) was calculated using equation (2)

$$L_i = \frac{1}{n}\sum_{1}^{n}\left[\log\left(\frac{\beta}{D_i}\right)\right]_n \qquad (2)$$

where β is the constant of 1.0 $cm^2/s$, n is the number of leach periods for which analytical results were obtained and $D_i$ is the effective diffusivity of constituent i. Effective diffusivity, $D$ ($cm^2$/sec) was calculated using equation (3):

$$D = \pi\left[\frac{a_n/A_o}{(\Delta t)_n}\right]^2\left(\frac{V}{S}\right)^2 T \qquad (3)$$

where $\Delta t_n = t_n - t_{(n-1)}$ is the duration of the n leaching interval (sec), $T = [\frac{1}{2}(t^{1/2}_n + t^{1/2}_{n-1})]^2$, leaching time representing the cumulative time in the middle of the interval n (sec).

### Unconfined compressive strength test

This test was carried out according to the American Standard Testing Material (ASTM) Test Method for Compressive Strength (CS) of Hydraulic Cement Mortars C190/C 109M-99 [15]. CS test is to determine the mechanical strength of the solidified spent catalyst-cement matrix in order to establish whether the matrix could be landfilled in layers or be used in construction, as the law permits. The spent catalyst-cement matrices were 50mm x 50mm x 50mm cubes. The strength measurements of the cubes were performed using a calibrated hand operated hydraulic compression apparatus (model ELE) on the 7th, 14th and 28th days of curing. It was not performed on the first day, because the cubes were not totally cured, some were still in paste form. The total maximum loads were recorded at the point of fracture on the cubes.

The loads were calculated as of equation (4)

$$f_m = \frac{P}{A} \qquad (4)$$

where $fm$ is the compressive strength in MPa, P is the total maximum load in Newtons and A is the area of loaded surface ($mm^2$).

## RESULTS AND DISCUSSION

### Physical and chemical properties of spent catalyst

Table 2 lists the physical and chemical properties of the spent catalyst. The spent catalyst is a greenish yellow solid. The original colour of the catalyst is yellowish. The greenish colour of the spent catalyst is due to the mixture of blue and yellow colours, whereby the blue-green color is the colour of $V^{4+}$ and $FeSO_4$ generated during the oxidation process of the sulfuric acid production [16]. Fe is not an original element of the spent catalyst. It is the product of steel pipe deterioration which was sucked from the early process stage and deposited on the spent catalyst. The moisture content of the spent catalyst was 4%, which is reasonable because the catalyst must be kept away from moisture, as this will accelerate deactivation of the catalyst. Specific gravity of the spent catalyst was 1.63. The pH of the leachate generated from mixing of spent catalyst with distilled water was around 1.3, which is due to the solubility of $V_2O_5$ that dissolves slightly in water to give an acidic solution [17].

From the acid digest, the metal components of the spent catalyst in the leachate were determined. Table 3 shows that spent catalyst contained K (839mg/l) V (356mg/l), Na (99mg/l), Al (44mg/l), Ca (23mg/l), Fe (13mg/l), Mg (13mg/l) and Pb (0.7mg/l). When compared with Malaysian EQA and TCLP standard threshold limits, it was found that only Fe and Pb exceeded the limits. V, K and Na are the original material in the spent catalyst while Al, Ca, Fe, Mg and Pb were infiltrated impurities that poisoned the catalyst.

**Table 2.** Physical and chemical properties of the catalyst used in the sulfuric acid production

| **PHYSICAL PROPERTIES**[a] | |
|---|---|
| Colour | Greenish yellow |
| Moisture content (%) | 4 |
| Specific gravity | 1.6 |
| pH | 1.3 |
| **CHEMICAL PROPERTIES (%w/w)**[b] | |
| Vanadium pentoxide, $V_2O_5$ | 5-9 |
| Potassium sulfate, $K_2SO_4$ | 10-30 |
| Sodium sulfate, $Na_2SO_4$ | 1-7 |
| Silica, diatomaceous earth, $SiO_2$ | 55-70 |
| Silica, crystalline, $SiO_2$ | 1-5 |

[a] Properties of spent catalyst, from experiment

[b] Properties of catalyst, source: Haldor Topsoe A/S 2005

**Table 3.** Metal composition of spent catalyst after acid extraction

| **NO.** | **TESTED ELEMENTS** | **TEST RESULT (mg/l)** | **STANDARD (mg/l)** | |
|---|---|---|---|---|
| | | | **EQA*** | **TCLP**** |
| 1 | Barium | <0.5 | 100 | - |
| 2 | Cadmium | <0.01 | 1.0 | 0.02 |
| 3 | Chromium | 0.3 | 5.0 | 1 |
| 4 | Lead | 0.7 | 5.0 | 0.5 |
| 5 | Calcium | 23 | - | - |
| 6 | Aluminium | 44 | - | - |
| 7 | Magnesium | 13 | - | - |
| 8 | Manganese | 0.2 | - | 1.0 |
| 9 | Iron | 12.9 | - | 5.0 |
| 10 | Sodium | 99.2 | - | - |
| 11 | Copper | <0.1 | - | 1.0 |
| 12 | Potassium | 839 | - | - |
| 13 | Zinc | 0.3 | - | 2.0 |
| 14 | Vanadium | 356.1 | - | - |

*Regulatory limit stipulated in Malaysia Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulation, 1979, *Standard B*

**United States EPA regulatory limits for TCLP Test.

**TCLP results of the S/S treated sample**

The TCLP results of four metals of concern, which are V, Fe, Pb and Cd, are shown in Table 4. For untreated spent catalyst, it was found that Fe and Pb concentrations were 61mg/l and 0.07mg/l; exceeding the Malaysian Environmental Quality Act, Standard B limits. Cd from OPC was at a concentration of 1.2mg/l, which was above the limit as well. Due to no threshold limits stated in the Malaysian EQA or TCLP, a USEPA proposed water pollution standard for V was used for comparison [18]. V was at 625mg/l in the leachate, prior to treatment (Table 4).

Table 4. Summary of TCLP results for solidified matrix leaching in acetic acid leachant, with and without sodium silicate (SS) additive

| | **INITIAL pH (fixed)** | **FINAL pH** | **CONCENTRATION OF METAL IN LEACHATE mg/l** | | | |
|---|---|---|---|---|---|---|
| | | | **V** | **Cd** | **Fe** | **Pb** |
| **REGULATORY LIMIT** | | | | | | |
| for TCLP Test[a] | - | | - | 1 | - | 5.0 |
| Malaysia EQA[b] | 5.5-9.0 | | - | 0.02 | 5.0 | 0.5 |
| Allowable level[c] | - | | 0.07[c] | - | - | - |
| SC | 2.88 | 2.44 | 625.0 | Bdl | 60.80 | 0.70 |
| OPC | 2.88 | 11.86 | Bdl | 1.16 | Bdl | Bdl |
| **OPC: SC** | | | | | | |
| 30:70 | 2.88 | 8.63 | 553.0 | 0.06 | 0.03 | Bdl |
| 40:60 | 2.88 | 9.79 | 96.50 | 0.01 | 0.02 | Bdl |
| 50:50 | 2.88 | 9.97 | 146.0 | 0.01 | 0.05 | Bdl |
| 60:40 | 2.88 | 9.84 | 86.70 | 0.01 | 0.01 | Bdl |
| 70:30 | 2.88 | 11.53 | 1.10 | Bdl | 0.02 | Bdl |
| **SS:OPC: SC** | | | | | | |
| 7:23:70 | 2.88 | 6.57 | 845.0 | Bdl | 0.16 | Bdl |
| 6:34:60 | 2.88 | 7.23 | 472.0 | Bdl | 0.01 | Bdl |
| 5:45:50 | 2.88 | 9.09 | 123.0 | Bdl | Bdl | Bdl |
| 4:60:40 | 2.88 | 10.25 | 27.10 | Bdl | Bdl | Bdl |
| 3:67:30 | 2.88 | 10.90 | 4.92 | Bdl | Bdl | Bdl |

[a] United States EPA regulatory limits for TCLP Test.

[b] Regulatory limit stipulated in Malaysia Environmental Quality Act 1974, Environmental Quality (Sewage and Industrial Effluents) Regulation, 1979, *Standard B*

[c] Recommended level (Sun *et al.* 2001);

Bdl: Below detection limit

After the S/S treatment, a significant drop was found in the metal concentrations of the TCLP leachate. For all ratios of cement S/S, Cd concentration ranged below detection limit at 0.06mg/l, Fe was at 0.01 - 0.05mg/l while Pb was below detection level (DL). V concentration was also reduced from 553mg/l (OPC: SC ratio of 30:70) to 1.10mg/l (OPC: SC ratio of 70:30). The same trend was found when SS was added into the cement-based treatment. It was found that the Cd, Fe and Pb were almost below DL at all ratios (Table 4). However, SS addition reduced V stabilization, as V concentrations were higher in SS added treatments compared to control cement treatment alone.

The untreated spent catalyst demonstrated an acidic pH of 2.4, which conformed to the results of waste characterization. After the treatment, the acid neutralization capacity of cement raised the pH to a range of 8.6 - 11.5 (for plain cement treatment) and 6.6 - 10.9 (for SS added treatment). The pH of the leachate has an impact on leachability of the metals. Metal leachability became lower when pH of the leachate increased from 7. During the cement hydration process, metal hydroxides will be formed. Amphoteric metal hydroxides have lower solubility at pH 7.5-11 [19].

## American Nuclear Society (ANSI/ANS 16.1) (modified) results of the S/S treated sample

### Leaching rate

The leaching rate, $l$ (cm/day) was calculated according to Eq. (1) and a sample calculation for the leaching of V from cement: spent catalyst ratio of 60:40 is given in Table 5. Figure 1 (a) and (b) depicts the leaching rates of metals at SC:OPC ratio of 60:40 and SS:OPC: SC ratio of 4:56:40. It is important to note that, all the metal leaching rates at different SC:OPC ratios or SS:OPC: SC ratios followed the same trend. The leaching rate on the first day was the highest and this reduced gradually with the leaching day. The leaching rate for V decreased from 0.078 cm/day in the first interval, to 0.026 cm/day in the second interval, and decreased to 0.005 cm/day, 0.004 cm/day and 0.002 cm/day after the third, fourth and final intervals, respectively. Leaching rates of SS added sample (Figure 1b) was lower compared to plain OPC treated sample. V leaching rates at this treatment were also the highest, decreased from 0.049 cm/day in the first interval, to 0.016 cm/day in the second interval, 0.003 cm/day, 0.001 cm/day and 0.0003 cm/day in the third, fourth and final intervals. The high leaching rates of all metals on the first day are possibly due to surface wash off [20].

### Leachability Index ($L_i$)

The $L_i$ was calculated according to Eq. (2) and Eq. (3) and a sample calculation for V is provided in Table 6. The average leachability indices for all metals of concern in the treated samples are displayed in Table 7. All $L_i$ were above the guidance value of 6, indicating that the metals were well immobilized in the solidified samples [21]. V treated with OPC has $L_i$ of 7.27-9.51 compared to 6.35-8.97 when treated with SS added OPC. This meant that the addition of SS did not enhance immobilization of V (which is also shown in TCLP results). The $L_i$ of Cd was around 8 for both treatment methods. The $L_i$ for Fe and Pb for both treatment methods were as high as 11. This showed that Fe and Pb were encapsulated effectively in the solidified matrices.

### Unconfined compressive strength

Unconfined compressive strengths of all OPC: SC ratios and SS:OPC: SC ratios at 7th, 14th day and 28th day curing are shown in Figures 2a and 2b. For both treatment methods, the compressive strengths recorded were higher when more OPC was loaded. When comparing at each testing interval, OPC treated cubes were observed to exhibit a higher compressive strength, posing 60% and 110% higher than SS added samples, at 14th day and 28th day of curing. The unconfined compressive strength of OPC treated samples ranged at 0.6 - 0.8MPa, 0.7 - 2.0MPa, 1.1 - 4.2MPa, 1.3 - 10.6MPa and 3.8 - 10.9MPa at 30, 40, 50, 60 and 70% spent catalyst loading, respectively. Although all the compressive strengths were less than 61% of the control values, their values were higher than landfill dumping criteria of 0.414MPa.

### Cost

Cost analysis revealed that S/S is the most cost effective (30% of current costs) and efficient option compared to the current direct disposal at Kualiti Alam or recovery of vanadium. These results are presented elsewhere.

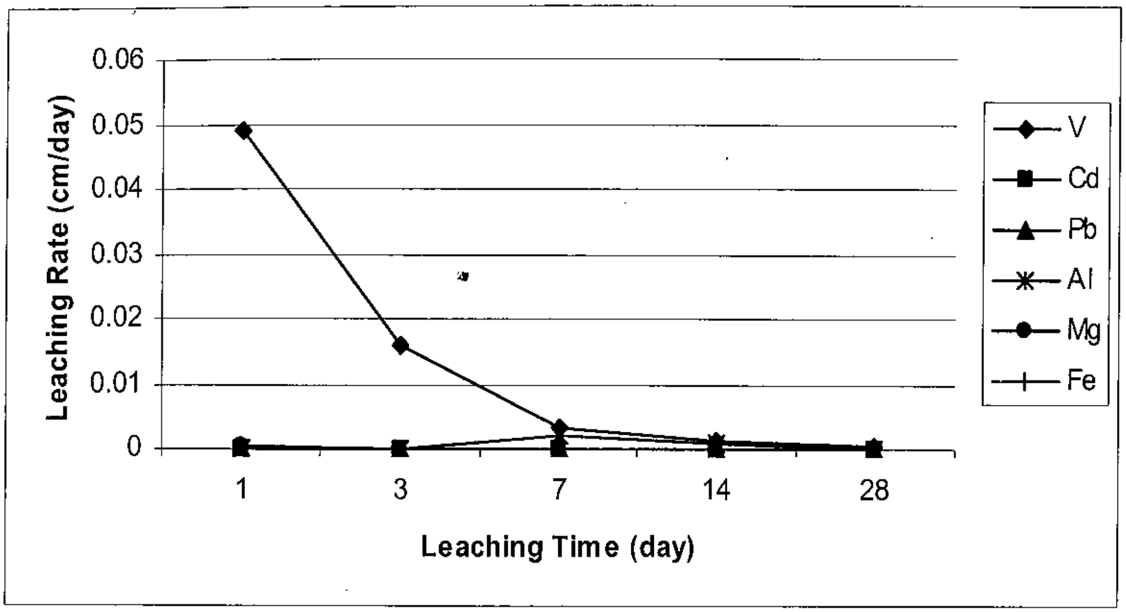

**Figure 1a**. Leaching rates of metals of concern at OPC:SC ratio of 60:40

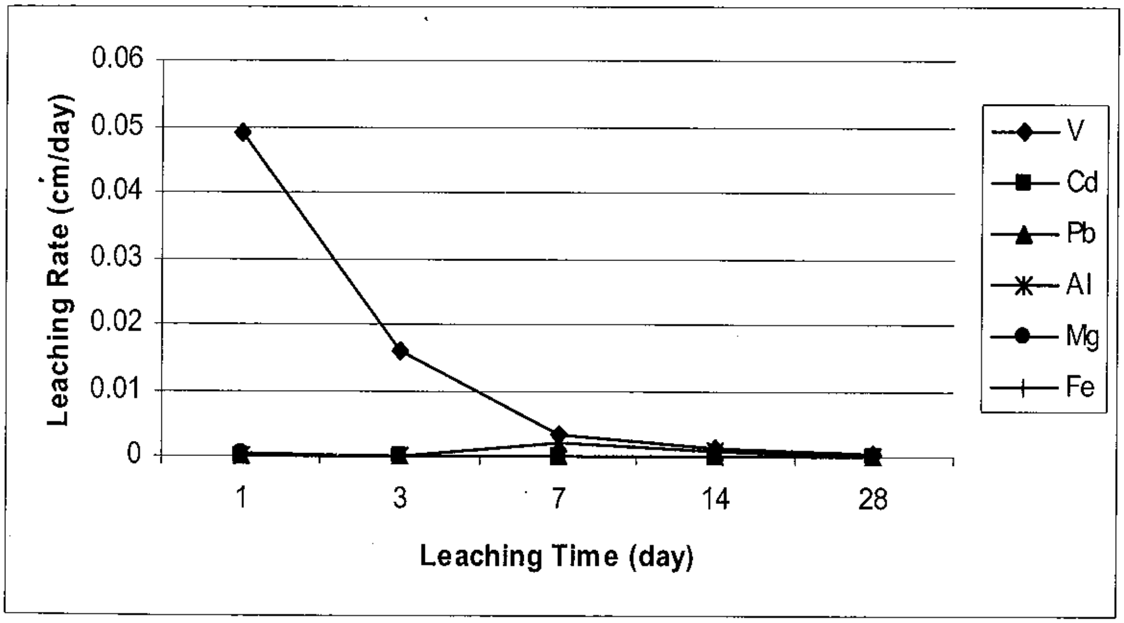

**Figure 1b**. Leaching rates of metals of concern at SS:OPC:SC ratio of 4:56:40

**Table 5.** Sample calculation for leaching rate of V, *l* (cm/day), in cement treated sample with cement: spent catalyst ratio of 60:40

| DURATION (DAY) | V IN LEACHATE (mg/l) | BLANK (CEMENT) (mg/l) | CORRECTED (mg/l) | $a_n$ (mg) | $a_n/A_o$ | V/S (cm) | *l* (cm/day) |
|---|---|---|---|---|---|---|---|
| a | b | c | d = b-c | e = d*0.65 | f = e/71.22 | g = 29.85/63.59 | h = f*g/a |
| 1 | 18.3 | 0.0443 | 18.3 | 11.9 | 0.1666 | 0.47 | 0.0782 |
| 2 | 12.4 | 0.1040 | 12.3 | 8.0 | 0.1122 | 0.47 | 0.0263 |
| 4 | 4.9 | 0.0046 | 4.9 | 3.2 | 0.0447 | 0.47 | 0.0052 |
| 7 | 6.0 | 0.0341 | 5.9 | 3.9 | 0.0544 | 0.47 | 0.0037 |
| 14 | 8.1 | 0.0008 | 8.1 | 5.3 | 0.0739 | 0.47 | 0.0025 |

$A_o$ = Amount of the constituent of interest initially present in the specimen = 71.22mg

*V* = Specimen volume, $\pi r^2 h = 29.855\ cm^3$

*S* = Specimen surface area, $2\pi r^2 + 2\pi rh = 63.589 cm^3$

**Table 6.** Sample calculation of Leachability Index ($L_i$) for V in cement treated sample with cement: spent catalyst at ratio of 60:40 at each interval

| DURATION (DAY) | $a_n/A_o$ | V/S (cm) | LEACHING DURATION, Δt (s) | T (s) | $(a_n/A_o)(1/\Delta t)$ cm | D ($cm^2/s$) | $L_i$ |
|---|---|---|---|---|---|---|---|
| a | b | c | d = 24*3600*a | f | g = b/d | $h = \pi g^2 c^2 f$ | i = log (1/h) |
| 1 | 0.1666 | 0.4695 | 86,400 | 21,600 | 1.93E-06 | 5.56E-08 | 7.25 |
| 2 | 0.1122 | 0.4695 | 172,800 | 125,894 | 6.49E-07 | 3.68E-08 | 7.43 |
| 4 | 0.0446 | 0.4695 | 345,600 | 251,788 | 1.29E-07 | 2.91E-09 | 8.53 |
| 7 | 0.0544 | 0.4695 | 604,800 | 466,192 | 9.00E-08 | 2.62E-09 | 8.58 |
| 14 | 0.0739 | 0.4695 | 1,209,600 | 881,258 | 6.11E-08 | 2.28E-09 | 8.64 |

Average L value of each interval, $L_i$ = (7.25 + 7.43 + 8.53 + 8.58 + 8.64) / 5 = 8.09

**Table 7.** Average leachability indices ($L_i$) of V, Cd, Fe and Pb at OPC: SC and SS: OPC: SC treatment ratios

| | AVERAGE $L_i$ | | | |
|---|---|---|---|---|
| | **V** | **Cd** | **Fe** | **Pb** |
| **OPC:SC** | | | | |
| 30:70 | 7.27 | 8.49 | 14.06 | 11.54 |
| 40:60 | 7.61 | 8.35 | 15.32 | 12.14 |
| 50:50 | 7.67 | 8.42 | 14.29 | 11.49 |
| 60:40 | 8.09 | 8.64 | 14.10 | 12.19 |
| 70:30 | 9.51 | 9.24 | 13.15 | 11.01 |
| **SS:OPC:SC** | | | | |
| 7:23:70 | 6.35 | 7.02 | 12.17 | 12.41 |
| 6:34:60 | 7.03 | 8.10 | -* | 12.00 |
| 5:45:50 | 8.32 | 8.68 | 16.57 | 11.56 |
| 4:56:40 | 8.92 | -* | 13.54 | - * |
| 3:67:30 | 8.97 | -* | 12.58 | - * |

* The metal concentration was below detectable limit. Guidance value of $L_i$ is 6.

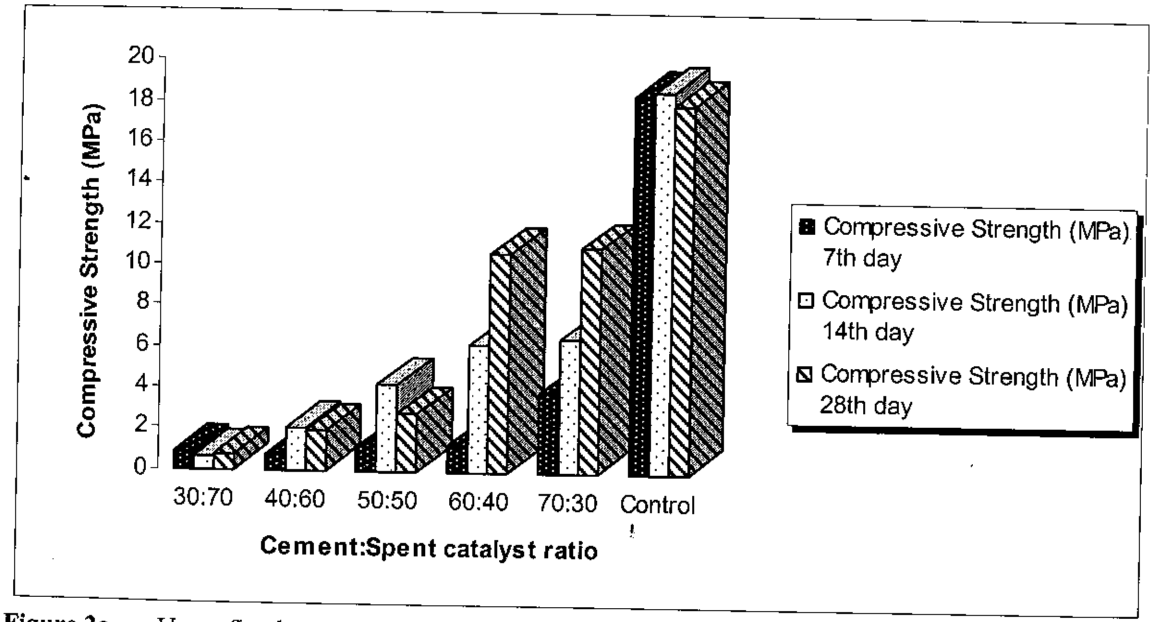

**Figure 2a.** Unconfined compressive strength for OPC: SC ratios

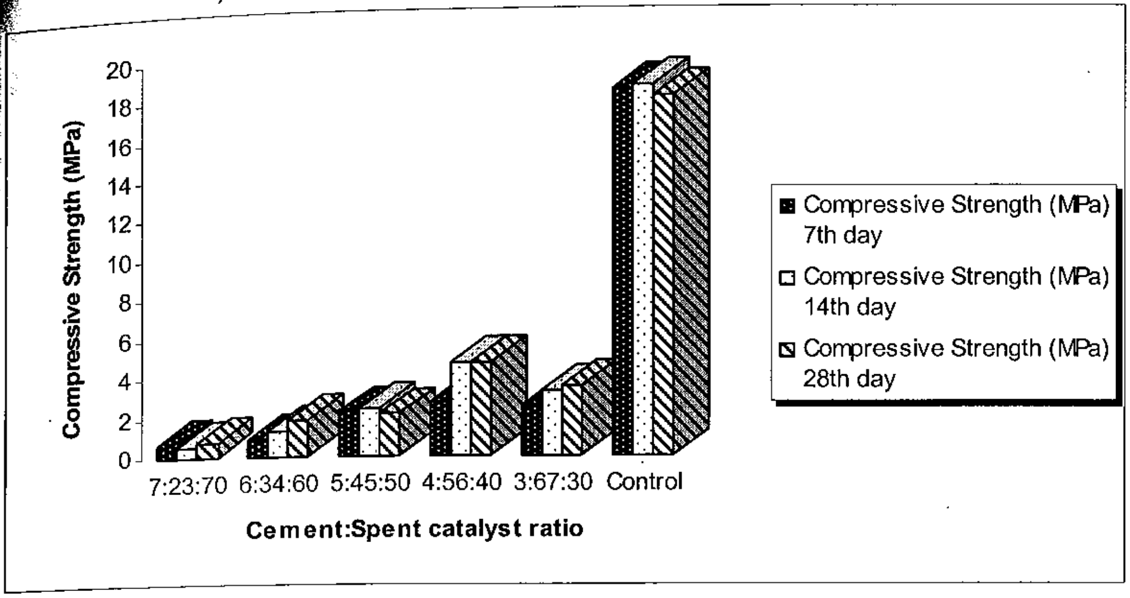

**Figure 2b.** Unconfined compressive strength for SS:OPC:SC ratios

## CONCLUSION

Spent catalyst contained metals above the Malaysian EQA and TCLP Standards of disposal. TCLP and ANS data proved that Solidification/stabilization using cement with or without sodium silicate was effective in the treatment of spent catalyst in containing the metal elements of concern to within the disposal limits. Sodium silicate (SS) usage did not enhance the stabilization capacity. Unconfined compressive strength of the solidified matrix showed that the treated waste matrix could be dumped safely into secure landfill or used as construction material, if the law permits.

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