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Recovery of heavy metals and stabilization of spent hydrotreating catalyst using a glass–ceramic matrix

Darren Delai Sun*, Joo Hwa Tay, Hee Kiat Cheong,
Dickson Lai Kwok Leung, GuangRen Qian

Environmental Engineering Research Centre, School of Civil and Structural Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

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Abstract

Chemical analysis of spent Co/Mo/ γ -Al₂O₃ catalyst revealed the presence of carbon, molybdenum, sulfur, vanadium and cobalt at levels of 16.0, 10.9, 7.3, 4.6 and 4.0 wt.%, respectively. It was found that calcination at 500°C provides an effective solution for the removal of carbon and sulfur and this generates the oxide form of the heavy metals. The removal of these heavy metals can be achieved through a two-stage leaching process. During the first stage, in which concentrated ammonia is used and it has been found that this process can be successful in removing as much as 83% (w/v) Mo. In a second stage, it was found that using 10% (v/v) of sulfuric acid, it was possible to account for up to 77% (w/v) Co and 4% (w/v) Mo removal. Leaching test results indicated that the vanadium present in the heated spent catalyst was almost stabilized but the molybdenum and cobalt were not. The combination of two solid wastes, ladle furnace slag (LFS) and treated residue of spent catalyst, could be used for making a high value-added anorthite glass–ceramic materials. Further leaching tests showed that ceramic glass materials provided a very effective method of Co, Mo and V heavy metals stabilization resulting in a product with a possible commercial value. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Anorthite glass–ceramics; Catalyst; Ladle furnace slag; Leaching; Heavy metals; Stabilization

1. Introduction

Co/Mo/ γ -Al₂O₃ and Ni/Mo/ γ -Al₂O₃ as catalysts are commonly used for hydrotreating process of heavy crude oil in the petroleum industry. This process results in the generation of spent catalysts that contain various heavy metals. Partial or complete regeneration

* Corresponding author. Tel.: +65-7906-273; fax: +65-7910-676.

E-mail address: ddsun@ntu.edu.sg (D.D. Sun).

of the spent hydrotreating catalysts can be carried out depending on the nature of desired reuse of the product [1]. In the long term, the regeneration of these catalysts will become impossible due to irreversible deactivation. Therefore, there is a need to find a reliable method for safe disposal or economical reuse of these toxic spent catalysts [1,2].

Land disposal is currently the most cost-effective solution for disposal of the wastes [2,3], but in Singapore, this method will soon become a very expensive option. Limited space and stringent environmental policies make it feasible to look into alternative ways to dispose of spent catalysts waste with a view to reuse. Generally, there are three possible ways to treat these spent catalysts [4]. The first method involves the total recovery or selective removal of metal contaminants. The recovery of the metals in the spent catalysts has been shown possible, but solid waste residues containing high concentrations of heavy metals above environmentally acceptable level can be expected [3]. Thus, a second treatment method considered total removal of metals together with stabilization and encapsulation of the spent catalyst [5]. However, a third method has been suggested to find alternatives for reutilizing the catalyst for producing a value-added product is more important than simple stabilization and encapsulation for land disposal [1,6,7].

Currently, many alternatives have been developed to transform spent catalyst containing heavy metals into a useful product. Bitumen concrete and polyethylene [5,8–11] can yield protection against leaching of heavy metals if they are used to encapsulate solid wastes with an impervious layer of sealant. However, this material is unsuitable in an acid environment. Ceramic and various types of glasses are the materials commonly used for stabilization, are resistant to leaching as well as breakage [12].

Glass–ceramics are crystalline materials formed through the controlled devitrification of glass [13,14]. Their structures are characterized by fine-grained, randomly oriented crystals with some residual glass without voids, microcracks, or other porosity. Anorthite ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) has been known for its insulating properties [15]. If anorthite mineral is introduced to unique microstructure of glass–ceramic as its predominant phase, formed anorthite glass–ceramic would have high dielectric constants and dc volume resistivity coupled with low loss tangents and, consequently, would be competitive with commercial electrically-insulating materials. A number of reports have been published on anorthite glass–ceramics using waste materials such as coal ash, sewage sludge ash and others [16–18]. However, the cost involved is high and in order to reduce the cost, it is necessary to generate value-added products from selected hazardous waste or industrial waste. Ladle furnace slag is an industrial waste, which is generated in large quantities during the steel making process, is currently being disposed of as a waste material; the dumping fee is high, chemically it is richer in CaO and SiO_2 but lower in Al_2O_3 and Fe_2O_3 . Therefore, the combination of two solid wastes, LFS and treated spent catalyst rich in Al_2O_3 , would be favorable to form high value-added anorthite glass–ceramic materials. Taylor and Bull [19] reported that the anorthite phase can easily form a solid solution with divalent metal oxides MgO, SrO, CdO and PbO, whose article will exhibit physical properties modified from those of simple anorthite assemblage. Considering the presence of heavy metal such as CoO and MoO_3 in the spent catalyst residues, this process represents a new concept in which a hazardous industrial waste is being used to treat another industrial waste to produce a value-added product.

This present study is exploring the possibilities for recovering heavy metals is from spent Co/Mo/ γ -Al₂O₃ hydrotreating catalyst and stabilizing the non-recovered heavy metals by using LFS to produce an anorthite glass–ceramic material.

2. Experimental methodology

The Co/Mo/ γ -Al₂O₃ catalysts used in this investigation were provided by the Singapore Refinery Company. The recovery of heavy metals from this catalyst was carried out using a bench-scale leaching recovery apparatus. This apparatus consist of a conical flask to hold the mixture of liquid leachate, spent catalyst and a stirrer. The treatment process had two stages. In the first stage, ammonia solution was used to recover molybdenum while sulfuric acid was used to recover cobalt in the second stage. The leachate sample was filtered and analyzed by atomic absorption spectrometer (Perkin Elmer-AAS) and using an inductively coupled plasma atomic emission spectrometer (Perkin Elmer ICP-AES 400). The percentage removal of metals was then calculated and compared to standard solutions provided by British Drug House (BDH). All other chemicals were of analytical grade provided by Ajax Chemicals.

Anorthite glass–ceramic was made from the residue of spent Co/Mo/ γ -Al₂O₃ catalyst, LFS and quartz sand together with a suitable nucleating agent. The LFS used in this study is a by-product of the steel making industry and was provided by NatSteel Ltd., Singapore. Table 1 lists the chemical composition of the raw material used in this investigation as well as the theoretical composition of some glass–ceramics. Two powder mixtures of glass–ceramic A and B (as shown in Table 1) were prepared and pressed into small batches. Mixture A contained the nucleating agent TiO₂; mixture B did not contain any additional nucleating agent. Using the petrographical method [16], the batches were first melted in a high temperature electric furnace at 1300°C for 3 h after which the melts were cooled slowly inside the furnace in order to form anorthite glass–ceramic. The phases of the resulting samples were analyzed by a Siemens powder X-ray diffraction (XRD) analyzer.

Table 1
Chemical composition of raw materials and glass–ceramic

	Major composition				
	Raw materials			Glass–ceramic (theoretical)	
	Treated catalyst (%)	Ladle furnace slag (%)	Sand (%)	A (%)	B (%)
SiO ₂	–	28.20	>98	35.48	38.98
Al ₂ O ₃	90.44	9.22	–	32.17	33.28
Fe ₂ O ₃	–	0.93	–	–	–
CaO	–	52.49	–	15.21	19.57
MgO	–	5.46	–	1.61	2.13
TiO ₂	–	0.77	–	10.00	–
Co	1.33	–	–	–	–
Mo	1.69	–	–	–	–

The toxicity characteristics leaching procedure (TCLP) test method [20] was used to evaluate the leachable behavior of heavy metals from spent Co/Mo/ γ Al₂O₃ catalyst and the stabilization of the treated glass–ceramic product. The leachant fluid used in TCLP procedure is an acetate/acetic acid buffer solution with a pH 4.93. Samples (100 g) were put into a standard plastic container together with 2000 ml of leachant. The container was then rotated at 18 rpm for 24 h. The leachates were filtered through a 0.45 μ m glass fiber filter and analyzed using the AAS.

3. Results and discussion

3.1. Recovery of heavy metals in spent catalyst

According to the supplier, the spent catalyst originated from a hydrotreating–cracking reactor. It was in the form of a black dust coated pellet. The chemical analysis of the catalyst is shown in Table 2.

The results revealed that the carbon, sulfur, cobalt, molybdenum and vanadium were major contaminants on the spent catalysts at 16.0, 7.3, 4.0, 10.9 and 4.6 wt.%, respectively. From the analytical data, it is clear that the spent catalyst contains high level of carbon and sulfur in addition to heavy metals cobalt and molybdenum. This high level of carbon and sulfur could be effectively removed by calcination at 500°C for 2 h to provide mixed oxides formation and MoO₃ sublimation. After the calcination process, the presence of vanadium was found to be negligible. This result may be due to the low melting point of vanadium oxide [1]. Thus, a baghouse may be required for the emission control of vanadium oxide dust in industrial practice.

Powder XRD analysis of the spent Co/Mo/ γ Al₂O₃ catalyst after calcination is shown in Fig. 1. From the results, one can see that the main phase of this spent catalyst after calcination was well crystallized γ Al₂O₃. CoMoO₃ compound was also detected.

Molybdenum may be in the form of mixed oxides after calcination at 500°C and may be dissolved in an alkaline solution unlike cobalt oxide [21]. Based on this information and from a cost point of view, a two-stage leaching process was suggested for recovering the metals: cobalt and molybdenum. Therefore, a first stage leaching procedure with an alkali was used to dissolve MoO₃, followed by the use of acidic media to recover the unreacted CoO [21]. In both cases, some substrate is dissolved, since γ Al₂O₃ is soluble in acidic as well as in a basic medium. However, γ Al₂O₃ has a lower solubility at a pH of approximately

Table 2
Chemical analysis of contaminants from Co/Mo/ γ Al₂O₃ catalyst

Contaminant properties	Fresh	Spent	After calcination
Carbon (wt.%)	–	16.00	–
Sulfur (wt.%)	–	7.30	0.40
Vanadium (wt.%)	–	4.60	0.20
Cobalt (wt.%)	2.70	4.00	5.80
Molybdenum (wt.%)	10.50	10.90	13.00

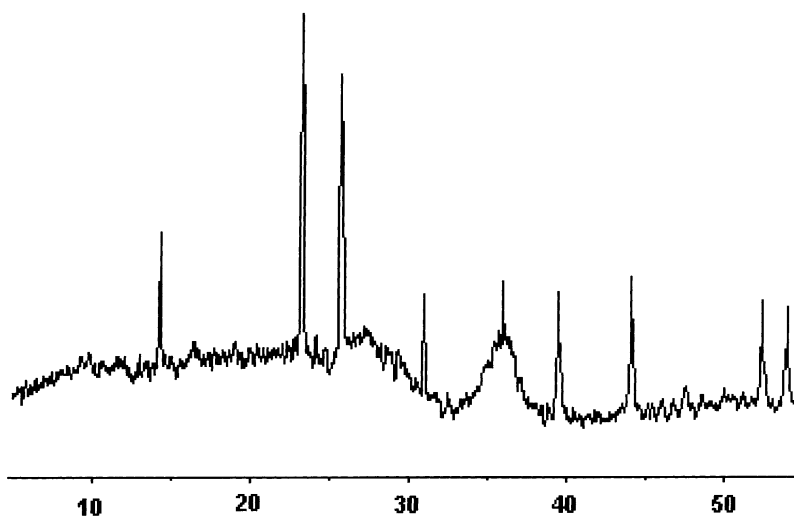


Fig. 1. Powder X-ray diffraction analysis results of spent Co/Mo/ γ -Al₂O₃ catalyst after calcination.

5 [22]. For the leaching process, concentrated ammonia and sulfuric acid were selected as the leaching reagents due to economic considerations.

Experimental results showed that approximately 83% (w/v) of the Mo could be removed during this first stage of the leaching process. Similarly, using 10% (v/v) of sulfuric acid could lead to the recovery of about 77% (w/v) of Co and 4% (w/v) of Mo after the second stage leaching process. These results confirmed the results obtained by Sun et al. [3,5]. This confirmation indicated that different batches of spent Co/Mo/ γ -Al₂O₃ catalyst could be treated by using the same method and achieve the same results. The effects of leaching time, alkali concentration and acid concentration for Co and Mo recovery are shown in Fig. 2. The catalyst:leachate ratio used was 1:25. The leaching process was carried out at room temperature.

After a two-stage leaching process, the residual solids in the flask were retrieved, washed with distilled water and dried. The resulting residual solids and initial spent catalyst samples were then tested for stability using the toxicity characteristics leaching procedure (TCLP). The criterion for the TCLP is that if the leachate concentration of any listed constituent exceeds 100 times, the drinking water standard (in the United States), the waste is termed “hazardous” under US LPA regulation. Due to the unavailability of an existing standard listing, the permissible concentrations of V and Mo level in drinking water, the proposed level recommended by Sittig [23] was chosen as the standard to be followed. The TCLP results are shown in Table 3.

As it can be seen from Table 3, the calcination process followed by the two-stage leaching process provided an effective treatment for molybdenum and cobalt recovery. However, the concentration of these heavy metals is still high in the residue and exceeds the allowable level proposed by Sittig [23]. Therefore, the waste still requires an effective means of disposal because of these catalyst residues.

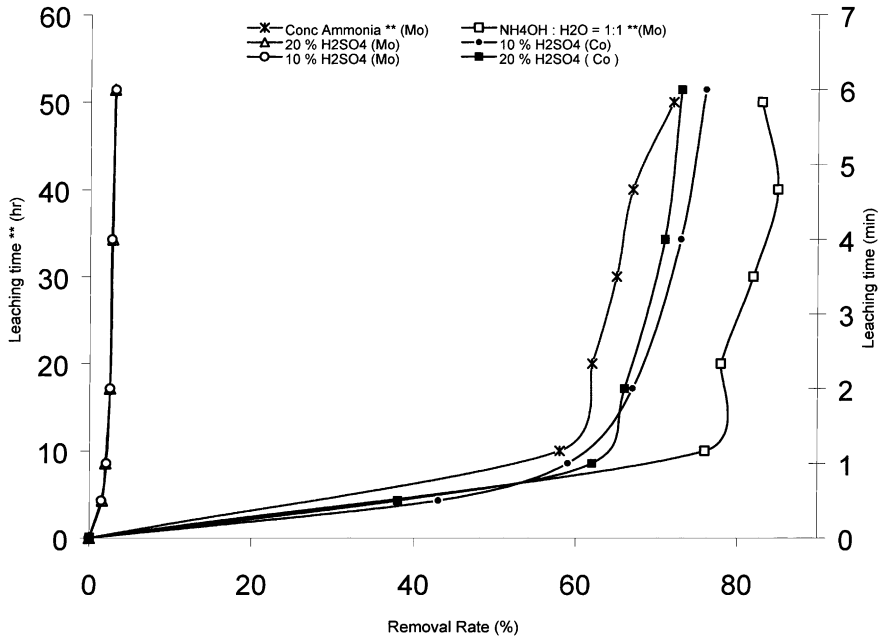


Fig. 2. Effect of leaching time, alkali concentration and acid concentration for the recovery of cobalt and molybdenum.

3.2. Fixation of heavy metals in anorthite glass–ceramic

In order to provide a cost-effective solution for the safe disposal of these residues, there was a need to find an alternative solution to land disposal. From a cost point of view, to produce a value-added material to treat these heavy metals using another industrial waste would be the perfect solution. A literature survey revealed the possibilities of producing an anorthite glass–ceramic material of economic value from several industrial wastes [16–18].

Anorthite glass–ceramic is being used currently in the electronic industry as an electrically-insulating material [24]. With this information, it was thought that using LFS to treat the spent catalyst residues together with quartz sand, a glass–ceramic material could be produced. LFS is a by-product of steel manufacturing industry. The powder XRD results are

Table 3
Toxicity characteristics, leaching procedure test results for spent Co/Mo/ γ Al₂O₃ catalyst

Metals in TCLP leachate (ppm)	After leaching	Before leaching	Allowable level [23]
V	0.2	31.0	0.7
Co	44.0	550.0	0.1
Mo	42.5	1056.0	7.0

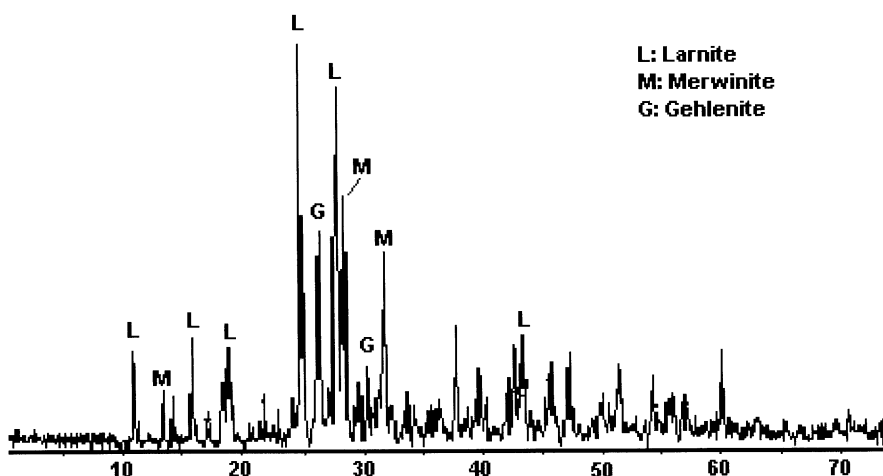


Fig. 3. Powder X-ray diffraction analysis result of ladle furnace slag.

shown in Fig. 3. It can be seen that the main minerals of this slag are based on calcium-rich phase, larnite ($2\text{CaO}\cdot\text{SiO}_2\text{--C}_2\text{S}$), merwinite ($3\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2\text{--C}_3\text{MS}_2$) and gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\text{--C}_2\text{AS}$). These main phases do not have any binding properties at ambient temperature and this classifies the LFS as a solid waste with no commercial value [9]. However, these calcium-rich phases are a potential source of calcium oxide and silica oxide that could be used in synthesizing anorthite glass–ceramic.

In design mixtures of anorthite glass–ceramic, mixtures A and B contained 38 and 42% LFS together with 27 and 30% of sand. The Al_2O_3 needed by anorthite phase was supplied by the treated residue of spent $\text{Co/Mo}/\gamma\text{Al}_2\text{O}_3$ catalysts which accounted for 25 and 28% in mixture A and mixture B, respectively.

To produce effective internal nucleation and glass–ceramic formation, normally a nucleating agent has to be added. TiO_2 is a nucleating agent that is commonly used in the glass–ceramic industry. Mixture A in Table 1 contained 10% TiO_2 whereas in mixture B, no nucleating agent was added. The melting temperature of common anorthite glass–ceramic is usually greater than 1400°C even reaching 1600°C [19]. However, it was found that both mixture A and mixture B started to melt at 1200°C and were fully melted at 1300°C . It is believed that this low melting temperature might be related to the existence of the calcium silicate phase and transition heavy metals in LFS and spent catalyst residues.

When the melting body with an anorthite composition was slowly cooled from 1300°C in the furnace, crystallized phase formation began to occur. A glass–ceramic product with numerous crystals and well distributed in a blue glass matrix was formed at ambient temperature. As compared to mixture A, mixture B contained more glass matrix than mixture A by macrography. Furthermore, the convex widen peak nearby the 30° mark in the XRD pattern of mixture B shown in Fig. 4, further confirmed the above observation. The results shown in Fig. 3 also indicated that the main crystallized phase formed in both sample A and sample B is only anorthite CAS_2 , which corresponds to the peaks at 4.04, 3.21, 3.18, 3.00 \AA . This result suggested that the combination of LFS and the treated residue catalyst could be

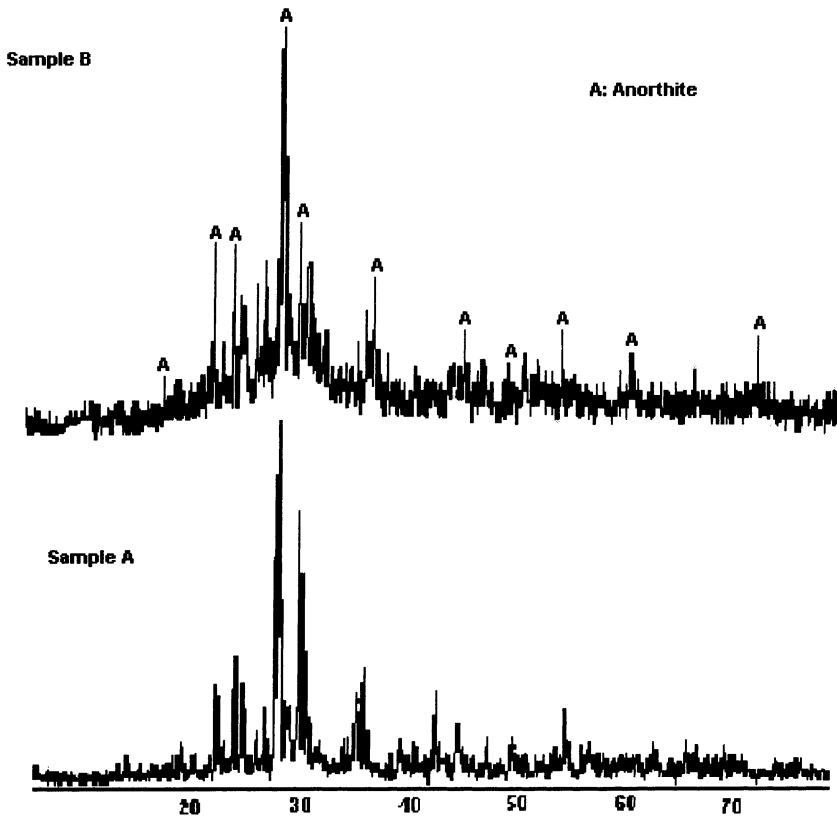


Fig. 4. Powder X-ray diffraction analysis results of anorthite glass–ceramic used for the stabilization of heavy metals.

used for producing value-added anorthite glass–ceramic material. Sample B contained the same main anorthite phase as sample A although its mixture did not have any nucleating agent. This result suggests that the transition heavy metals in samples such as cobalt, not only played a role of coloring agent to form a blue glass matrix but also acted as a nucleating agent to accelerate the nucleation of anorthite. It is also an interesting point, to note the failure of the nucleating agent (TiO_2) to help in producing a better glass matrix in mixture A. Further studies to investigate this phenomenon is required.

To examine whether anorthite glass–ceramic material could effectively stabilize the heavy metals present in the treated spent $\text{Co/Mo}/\gamma\text{Al}_2\text{O}_3$ catalysts residues, a TCLP leaching test was carried out. The results from Table 4 showed that TCLP leaching values of Mo, Co heavy metals from anorthite glass–ceramic material were only 10–150 $\mu\text{g/l}$ and that V metal could not be detected by the AAS. These values were much lower than TCLP allowable level, which indicates that the novel anorthite glass–ceramic made from treated residue of catalyst and LFS can be considered as an environmental friendly material that can be used for commercial purpose.

Table 4

Toxicity characteristics leaching procedure test results for spent Co/Mo/ γ -Al₂O₃ catalyst residues and anorthite glass–ceramic

Heavy metals	Leaching from treated residue of catalyst (ppm)	Leaching from glass–ceramic (ppm)	TCLP allowable level (ppm)
Mo	42.50	0.15	7.00
Co	44.00	0.02	0.07
V	0.20	Not detected	0.70

The US EPA TCLP criterion used in this study requires that the leachate concentration of any listed constituent should not exceed 100 times the drinking water standard. Otherwise, the waste is termed “hazardous”. Unfortunately, the relevant standards do not list V, Mo and Co. In this regard, the permissible limits of heavy metals concentration in drinking water, as recommended by Sittig [23], have been taken as a relevant water quality standards. The TCLP leaching results obtained in this investigation are well below the proposed allowable level and would unlikely be affected by the standards.

The negligible leaching properties of anorthite glass–ceramic can be attributed to the effective stabilization of anorthite phase and glass matrix on Co, Mo and V heavy metals. Anorthite belongs to a tectosilicate mineral of feldspar group. The silicon and aluminum in the anorthite structure occupy the centers of interlinked tetrahedrons of SiO₄ and AlO₄. These tetrahedrons connect at each other to other tetrahedrons forming an intricate, three-dimensional, negatively charged Al–Si frameworks. Calcium cations in anorthite structure are eight- or six-fold coordinated to set within the voids in this structure. The radius of Ca²⁺ and Co²⁺ are 1.00 and 0.74 Å, respectively. According to the theory of crystalline chemistry [25], Ca and Co have the same divalent positive charge but their ratios of cation and anion ratio are within the range of six-fold coordination. Thus, it may be inferred that Ca²⁺ in the anorthite structure can be easily replaced by Co²⁺ but this replacement is finite due to size factor of two cations. Legrouri et al. [26] reported that the substitution limit of some Ca²⁺ by Co²⁺ in Ca_{3-x}CO_x(PO₄)₂ structure could be up to $x = 0.31$. On the other hand, molybdenum has been widely used to synthesize oxide glasses with semiconducting properties. Khattak et al. [2] reported that Mo⁵⁺ ions are mainly gathered in the tetragonally distorted octahedron of glass matrix. As described above, anorthite glass–ceramic is a composite material made of both anorthite phase and glass matrix, in which Co²⁺ would replace Ca²⁺ in anorthite phase and Mo⁵⁺ would be combined into tetragonally distorted octahedron in glass matrix. Therefore, this analysis may explain the reasons of why anorthite glass–ceramic material can effectively stabilized the Co and Mo heavy metals.

4. Conclusion

Carbon and sulfur can be effectively removed from a spent hydrotreating catalyst by calcination at 500°C. This process also promotes the formation of the oxides of the heavy metals. The recovery of these heavy metals can be achieved through a two-stage leaching process. The first stage using concentrated ammonia can result in up to 83% (w/v) of Mo

recovery. In the second stage, involving the use of 10% (v/v) sulfuric acid, it was found that approximately 77% (w/v) Co together with 4% (w/v) Mo could be extracted from the catalyst. It was found that the combination of the two solid wastes, LFS and treated residue of spent catalyst could be used for making a value-added anorthite glass–ceramic material. Furthermore, leaching tests showed that Co, Mo and V heavy metals from treated residues of the spent catalyst could be effectively stabilized in this anorthite glass–ceramic material. This study revealed the possibility of using an industrial waste to treat another industrial waste to produce a high value-added product.

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