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Arshe Said Sanni Eloneva

# Assessment of feasibility of extracting different metals from spent steel converter slag



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Aalto University CCSP WP5, D514

Arshe Said Sanni Eloneva

Assessment of feasibility of extracting different metals from spent steel converter slag



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## Report Title: Assessment of feasibility of extracting different metals from spent steel converter slag

Key words: slag residue, vanadium, aluminum, extraction

#### Abstract

The objective of this study was to develop a solvent(s) which enables extraction of vanadium (V) and other recoverable metals from the residual slag of the Slag2PCC-method (in which  $CO_2$  mineralization is used to produce pure calcium carbonate from the steel converter slag). This would make it easier to find new utilization options for the spent slag, as leaching of the harmful elements could reduce. In addition, the method could at the same time gain more value by producing marketable products (e.g. catalysts from the dissolved metals).

It was found that calcium extraction clearly increases porosity of the slag, likely promoting metal extraction. However, none of the chosen solvents was selective for any of the elements selected for analysis. Sodium bicarbonate dissolved silica and vanadium quite selectively, although their concentrations in the solutions were quite small. In addition, none of the elements was dissolved in any significant amount, as the best extraction reached (calcium with 2 M aqueous solution of ammonium sulfate) was less than 20 %.

The next task is to continue the literature review for finding solvents for better metal extractions. Special focus is in extraction of vanadium from the spent steel converter slag.



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#### 1 Introduction

The objective of this study was to develop a solvent(s) which enables extraction of vanadium (V) and other recoverable metals from the residual slag of the Slag2PCC-method (in which CO<sub>2</sub> mineralization is used to produce pure calcium carbonate from the steel converter slag). This would make it easier to find new utilization options for the spent slag, as leaching of the harmful elements could reduce. In addition, the method could at the same time gain more value by producing marketable products (e.g. catalysts from the dissolved metals). Compared to ores, the residues have a number of advantages, e.g. low cost, high reactivity due to their chemical instability and their availability near to the production site. Hydrochloric acid and sulfuric acid solutions are used for recovering vanadium from stone coal, [1-2]. But acid solutions will also dissolve the other elements in the slag. Therefore, in order to avoid this risk we used base solutions. Salts such us sodium chloride and alkali metal hydroxides NaOH were reported to increase the rate of dissolution of silica gel [3]. Sodium bicarbonate was reported to dissolve vanadium selectively [4]

Figure 1 shows a simplified scheme of the ideal method, in which the spent slag from the  $CO_2$  mineralization method Slag2PCC is used for production of valuable metals (vanadium (V), aluminum (AI) and silica (Si) as an example). This would be based on the so called chemical fractionation, in which metals in the residual slag (e.g. V, AI, Si) are extracted selectively by a chemical solvent according to their solubility in different solvents.



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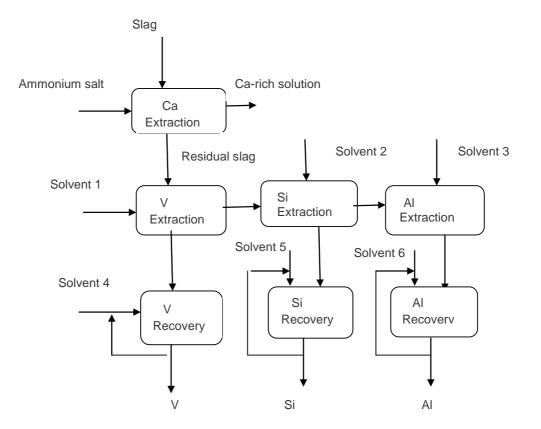


Figure 1.Metal recovery option scheme for the spent slag from the  $CO_2$  mineralization method Slag2PCC (V, Al and Si as an example).

#### 2 Methods

Residual steel converter slag from the extraction reactor (in which calcium was dissolved from the slag) was first washed with distilled water. This was done in order to remove any possible silica gel formatted on the surface of the slag residue as well as for removing any possible solvent residues. Silica gel is assumed to hinder the extraction of metals from the spent slag. After washing, 3 g of the wet slag residue (Table 1) was dissolved in 150 ml aqueous solutions of 1 and 2 M concentrations chloride (NaCl), sodium hydroxide (NaOH), of sodium sodium bicarbonate (NaHCO<sub>3</sub>) (1 M solution only) and ammonium sulfate  $((NH_4)_2SO_4)$ . The solutions were stirred by a magnetic stirrer for an 1 hour at 30 °C temperature. Solution samples of 5 ml were taken 5, 20, 40 and 60 minutes after addition of the slag. The solutions were immediately filtered and then sent for analysis. The concentrations of calcium (Ca), Si, V, iron (Fe), AI, manganese (Mn) and magnesium (Mg) in the filtered solution samples were measured with Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

Table 1. Contents of selected elements in the spent steel converter slag according to ICP-AES (wt-% (wet)).

Ca	Fe	Si	Mn	V	Al	Mg
20.2	10.1	9.2	2.4	2.0	1.1	1.0

It is assumed that high porosity would result in better metal extraction. Therefore porous structure of the steel converter slag, both before and after extraction of calcium was studied by  $N_2$  adsorption /desorption isotherms at 77 K<sup>1</sup>.

#### 3 Results

#### 3.1 Porosity

Porosity of the steel converter slag, both before and after extraction of calcium was studied by N<sub>2</sub> adsorption /desorption isotherms at 77 K as presented in Figure 2. It can be seen that the sample of the slag prior calcium extraction has no adsorption at all, demonstrating the absence of porosity in the original material. However, the extraction of calcium from the slag generates some pores. These open cavities of the slag residue give rise to a slight N<sub>2</sub> adsorption at low relative pressures which indicates the development of micropores. The BET (Brunauer-Emmett-Teller) method was used to indentify the surface area of the slag before and after extraction of calcium. Table 2 summarizes results from N2 adsorption / desorption tests. S<sub>BET</sub> presents the BET surface area of the sample, V<sub>0</sub> is the total volume of micropores in the sample and V<sub>t</sub> corresponds to the total pore volume (micropores + mesopores + macropores) in the sample.

<sup>&</sup>lt;sup>1</sup> Experiments were made by Dr. Joaquin Albero at University of Alicante Department of Inorganic Chemistry



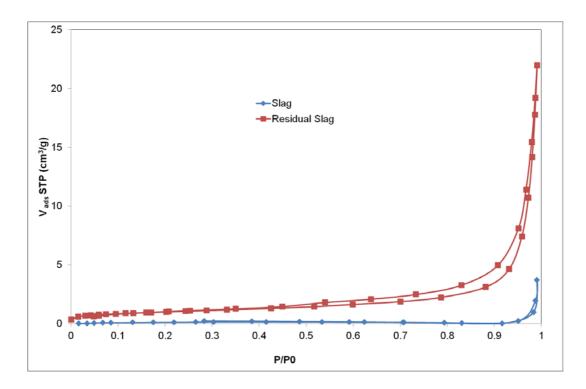


Figure 2.  $N_2$  adsorption/ desorption isotherms at 77 K for steel converter slag before (named as "Slag") and after (named as "Residual slag") extraction of calcium.

Table 2.  $N_2$  adsorption/ desorption isotherms at 77 K for steel converter slag before (named as "Original") and after ("Residual") extraction of calcium.

Steel converter slag sample	S <sub>BET</sub> (m²/g)	V <sub>0</sub> (cm <sup>3</sup> /g)	V <sub>t</sub> (cm <sup>3</sup> /g)
Original	0	0	0
Residual	5	0	0.03

#### 3.2 Metal extraction

Selected solvents were able to dissolve 3-13 % of the slag residue's vanadium within the 1 hour the experiments lasted (Figure 3). Both, 1 and 2 M aqueous solution of ammonium sulfate, as well as 1 M aqueous solution of sodium bicarbonate extracted more than 10 %, while other selected solvents dissolved less than 7 %.



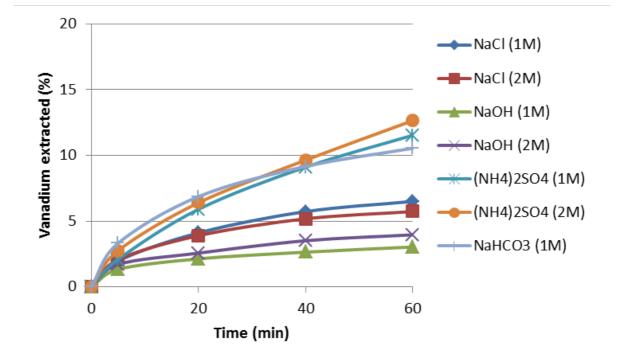


Figure 3. Dissolution of vanadium from the slag residue in aqueous solutions of selected solvents

Both aqueous solutions of sodium hydroxide (1 and 2 M) were able to dissolve ~5 % of the residue's aluminum, while its dissolution was insignificant in other solvents (Figure 4).

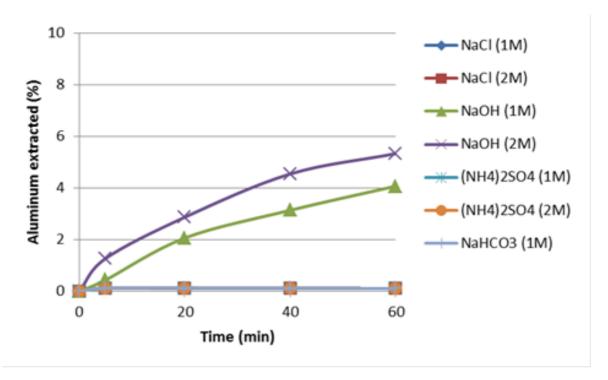


Figure 4. Dissolution of aluminum from the slag residue in aqueous solutions of selected solvents.



Both, 1 and 2 M aqueous solution of ammonium sulfate dissolved 13-16 % of the residual slag's calcium, while other solvents dissolved less than 5 % (Figure 5).

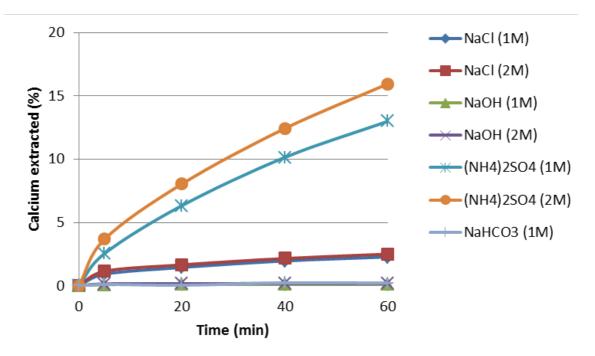


Figure 5. Dissolution calcium from the slag residue in aqueous solutions of selected solvents.

Dissolution of other measured elements was quite weak. Less than 4 % of silica, less than 1 % of manganese, 1 % or less of magnesium and less than 0.15 % of iron was extracted with any of the selected solvents.

Concentrations of the selected elements in the tested solvents within the experiment are shown in Figure 6. It can be seen that none of the solvents is selective for any of the elements selected for analysis. Nonetheless, sodium bicarbonate could be used to dissolve silica and vanadium almost selectively, giving a solution that contains ~40 mg/l silica and ~50 mg/l vanadium (Figure 7).



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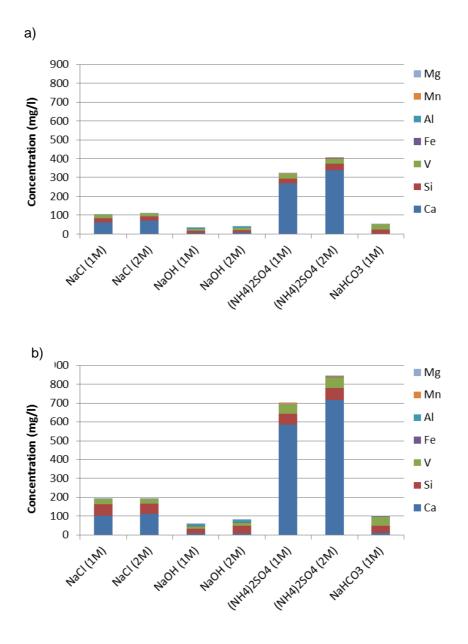


Figure 6. Dissolution of selected elements from the slag residue in aqueous solutions of various different solvents within a) 20 minutes b) an hour.

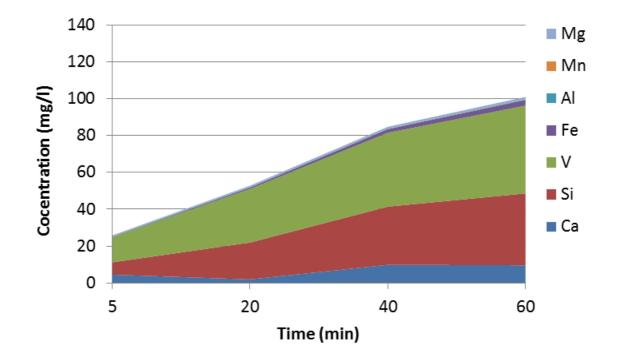


Figure 7. Dissolution of selected elements from the slag residue in 1 M aqueous solution of sodium bicarbonate.

### 4 Conclusions and future work

This report presents the current state of our research, in which the metal extraction from the residual slag of the Slag2PCC-method is investigated. It was found that calcium extraction clearly increases porosity of the slag, likely promoting metal extraction. However, none of the chosen solvents was selective for any of the elements selected for analysis. Sodium bicarbonate dissolved silica and vanadium quite selectively, although their concentrations in the solutions were quite small. In addition, none of the elements was dissolved in any significant amount, as the best extraction reached (calcium with 2 M aqueous solution of ammonium sulfate) was less than 20 %.

The next task is to continue the literature review for finding solvents for better metal extractions. Special focus is in extraction of vanadium from the spent steel converter slag. In addition, slag residue needs to be analyzed before it is washed with water, in order to find out how this washing affects the slag's properties.



#### 5 References

[1]. WANG Mingyu, XIAO Liansheng, LI Qinggang, WANG Xuewen, and XIANG Xiaoyan. Leaching of vanadium from stone coal with sulfuric acid Rare Metals Vol. 28, No. 1, Feb 2009, p. 1

[2]. T. D. Batueva and V. I. Karmanov. *Extraction of Vanadium(V) by* N',N'\_Dialkylhydrazides of Carboxylic Acids from Acidic Solutions Russian Journal of Inorganic Chemistry, 2011, Vol. 56, No. 6, pp. 986-990.

[3]. A. A. Palant, V. A. Bryukvin, and V. A. Petrova. Liquid-Liquid Extraction of Vanadium(V) from Sulfate Media with Diisododecylamine Russian Journal of Inorganic Chemistry, 2007, Vol. 52, No. 6, pp. 963-968

[4]. Zhao Zhuo, , Li Xiaobin, and Zhao Qingjie. Recovery of  $V_2O_5$  from Bayer liquor by ion exchange. Rare Metals Vol. 29, No. 2, Apr 2010, p. 115