CLEEN
Cluster for Energy and Environment

CCSP WP5, D531
Espoo 2014

Sanni Eloneva
William Zappa
Arshe Said

Report on progress with extracting vanadium from spent steel converter slag

ccsp
Carbon Capture and Storage Program

CLEEN LTD
ETELÄRANTA 10
P.O. BOX 10
FI-00130 HELSINKI
FINLAND
www.cleen.fi

ISBN XXX-XX-XXXX-X
ISSN XXXX-XXXX

Aalto University
CCSP WP5, D531

Sanni Eloneva
William Zappa
Arshe Said

Report on progress with extracting vanadium from spent steel converter slag

Aalto University
Espoo 2014

Report Title: Report on progress with extracting vanadium from spent steel converter slag

Key words: slag residue, vanadium, extraction

Abstract

The objective of this study was to develop a solvent(s) which enables efficient and selective extraction of vanadium (V) 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). The Slag2PCC-method could gain more value by producing marketable products (here vanadium) from the slag residue.

Neither the literature review nor results from our earlier experiments indicated anything very interesting to be tested for. However, couple of different acids, ammonium dihydrogen phosphate and sodium hydroxide was chosen to be tested. It was found that none of these solvents are suitable for dissolving vanadium efficiently and selectively from the residual slag. However, if economic way can be found to recover vanadium selectively from these solutions, then these solvents might be useful.

Espoo, November 2014

Table of contents

1 Introduction

1.1 Object of the study

The object of this study is to continue work on identifying valuable utilization options for the residual slag of the Slag2PCC-method method (in which CO_2 mineralization is used to produce pure calcium carbonate from steel converter slag). In a previous report (D514 Assessment of feasibility of extracting different metals from spent steel converter slag), research for developing a method for selective extraction of valuable metals from the residual slag was initiated. However, none of the mentioned solvents was selective for any of the elements selected for analysis (Ca, Si, V, Fe, Al, Mn, Mg). In this report, focus is on vanadium (V). First, a literature review on extraction of vanadium from steelmaking slags is made. Second, experience from one of our earlier projects, Slag2PCC Plus (2007-2009), as well as the results reported in our previous report (D514), concerning extraction of vanadium, are summarized. Next, these and literature findings are analyzed and suggestions on how to proceed are presented. Finally experiments are made and analyzed.

1.2 Literature review

The world's total amount of vanadium is estimated to be about 56.3 Mt (Ye, 2006). It exists mainly in the form of titaniferrous magnetite. Vanadium is usually produced from this mineral either directly via V-extraction processes or via iron- and steelmaking processes. Other vanadium containing raw materials are spent catalyst, petroleum residue and fly ashes, from which vanadium is produced via V-extraction processes.

Vanadium products include FeV-alloy, V_2O_5, V_2O_3, VN and metallic V. FeV-alloy is used mainly for the steel industry, while V_2O_5 and V_2O_3 are used for production of FeV. V_2O_5 is also widely used as a catalyst. VN is used for direct alloying of V and N, and V-metal is used in Al-V-Ti-alloy. Steel industry is the biggest consumer of vanadium (over 90 % (Roskill, 2013)). In 2012 global vanadium production grew up to ~74 000 t (estimate) (Polyak, 2013). For comparison, the amount of vanadium in disposed off BOF slag in Sweden alone amounts up to 5000 t per year (Ye et al., 2013). In steel industry, vanadium is used mainly in high-strength low-alloy steel (HSLA) products (Ye, 2006). Anticipating on development of HSLA steels, vanadium consumption is expected to continue increasing. Major vanadium producing countries are South Africa, China and Russia (Polyak, 2013). The annual average price for FeV in Europe, ranged from 24.786 to 25.475 $/kg in 2012.

Conventionally vanadium is extracted from its raw material (V-bearing magnetite concentrate, V-slag, fly ash, other V-bearing materials) either via alkali leaching, salt roasting or acid (H_2SO_4) leaching (ye, 2006). Water, alkali or acid leaching is used also after salt roasting. Prior precipitation of V_2O_5 solution purification is usually used. Salt roasting is done in order to change vanadium compound to a soluble form. The roasting process is done in rotary kiln for up to 10 hours at 800-1230 °C. Direct alkali or acid leaching generate huge amounts of residues and are hardly used, because of the environmental impact. Acid leaching is effective, but not selective for vanadium, while alkali leaching is less effective, but is selective. The latter also needs higher temperature and pressure. Vanadium sources described in Ye (2006) for direct leaching are U-V ore, catalyst, fly ash, boiler residue, of which only the first two are used for acid leaching.

Open scientific literature on leaching of vanadium from steelmaking slags is almost non-existent. Tavakoli et al. (2013) has summarized some important research studies on vanadium leaching from different resources. Among these, fly ash seems to be the most commonly tested material. Solvents used are H_2O, H_2SO_4, NaOH, NH_3, NH_4OH, NH_4Cl, Na_2CO_3, from which NaOH and H_2SO_4 were used in tests made with steel slag.

Steel slag used in the leaching experiments made with NaOH (at 140-240 °C) mentioned above and reported by Xiao et al (2010) contained jacobsite, titano-magnetite, fayalite and cristobalite. Therefore, it has a composition that is very different from the residual slag (or steel converter slag raw material) of the Slag2PCC method.

Steel converter slag used in the experiments made with H_2SO_4 mentioned above and reported by Aarabi-Karasgani et al (2010) contained portlandite, calcium iron oxide, calcium silicate (Ca_3SiO_5) and calcium vanadium oxide. Prior to leaching, the slag was roasted (at 1000 °C, 2 h, with 20% sodium carbonate). The roasted slag contained srebrodolskite, calcium iron oxide, calcium manganese oxide, sodium vanadium oxide and portlandite. Also here, the vanadium seems to be in a form different from the residual slag of the Slag2PCC method (or as in the steel converter slag used as raw material for the Slag2PCC method. (V-bearing phases will be presented in the next paragraph). However, a quite high vanadium recovery was achieved (~95 %) at the optimum leaching condition of 70 °C, S/L:1/15, 3 M solution, 150 min. Besides vanadium, also other elements were dissolved (Fe, Mn, Ca, Mg, Ti, Al and Si).

Van Zomeren et al. (2011) investigated changes in mineralogical and leaching properties of steel converter slag resulting from accelerated carbonation (at a relatively low CO_2 pressure of 0.2 bar). The slags used in their experiments (containing magnesio wuestite, free lime, portlandite, dicalcium ferrite, dicalcium silicate and magnetite) seem to be quite similar to that used as raw material in Slag2PCC method. The pH reduction caused by carbonation was found to lead to increased leaching of vanadium. The V-bearing di-Ca silicate was identified as the major source of leachable V. Another major phase containing vanadium was di-Ca ferrite. Therefore, it might be that if the leaching of calcium is very efficient in Slag2PCC method, part of the leachable vanadium is already dissolved during the extraction step i.e. preventing its downstream leaching from the residual slag. On the other hand, recovery of V from the Slag2PCC process solutions may be an option.

Yang-ge et al. (2010) compared leaching of vanadium from roasted and non-roasted residue of stone coal. It was found that leaching was easier from roasted than not roasted material. Direct leaching of vanadium from stone coal residue (88.78 % SiO_2, 1.7 % C, 0.93 % V_2O_5) was enhanced by increased concentrations of sulfuric acid (from 0.9 to 27 %), increased leaching temperature (from 40 to 90 °C) and increased leaching time (from 1 to 8 h).

Tavakoli et al. (2013) also studied the kinetics of V_2O_5 leaching. They found that although the reactions were fast in acidic media, the solubility of VO_2^+ was low. The solubility increased with decreasing pH (from pH 1.4 to 0.3) and temperature (from 90 to 30 °C). The solubility of vanadium was found to be greater in sulphuric acid than in nitric or hydrochloric acid at solution pH=1. Sulphate concentration in the solutions was also found to increase the solubility of vanadium. This was tested by adding sodium chloride and sodium sulphate separately to hydrochloric acid solutions. The improvement was believed to be due to the complexanation of vanadyl ion by sulphate. It was also shown that V_2O_5 can be leached in water and mild sodium hydroxide solutions at constant pH (pH 5-8). Under these conditions, temperature had a significant effect on leaching; complete dissolution was observed at 90°C. By increasing pH from 5 to 8, the kinetics of vanadium leaching was improved dramatically. Due to higher solubility of vanadium (IV) compared to that of vanadium (V) in acidic media, the use of reductive agent (sodium sulphite) increases leaching of vanadium pentoxide.

1.3 Leaching of vanadium from steel converter slag-experiments made in Slag2PCC Plus project

In our previous project, Slag2PCC Plus, we investigated the possibility to dissolve calcium selectively from steel converter slag, and optimize that. Therefore, quite a few common solvents were tested and besides calcium, concentrations of also certain other elements (including vanadium) were analyzed (Tveit et al., 2009).

It was found that vanadium was dissolved in aqueous solutions of propionic acid (CH_3CH_2COOH), acetic acid (CH_3COOH), ammonium sulfate ($(NH_4)_2SO_4$), ammonium dihydrogen phosphate ($NH_4H_2PO_4$), and nitric acid (HNO_3) (Figure 1). Solvents that did not dissolve any detected amounts of vanadium (≥1 mg/g of slag) were urea ($(NH_2)_2CO$), sodium hydroxide (NaOH), sodium chloride (NaCl), ammonium chloride (NH_4Cl), ammonium nitrate (NH_4NO_3), ammonium acetate (CH_3COONH_4), sodium acetate (CH_3COONa), diammonium hydrogen phosphate ($(NH4)_2HPO_4$), aluminum sulfate ($Al_2(SO_4)_3$), aluminum nitrate ($NH_4(NO_3)_3$) and sulphuric acid (H_2SO_4). Either 0.5, 1 or 2 molar aqueous solutions were used except in the case of ammonium dihydrogen phosphate and diammonium hydrogen phosphate (0.5 and 1 M), aluminum sulfate and aluminum nitrate (0.1 and 0.2 M), sulphuric acid (0.01, 0.05 and 0.1 M). In addition to 0.5, 1 and 2 M aqueous solutions of propionic acid and nitric acid, also 0.1, 0.2 and 0.3 M solutions were tested.

Nitric acid, acetic acid and propionic acid all dissolved significant amount of slags vanadium. However, many other elements were dissolved as well (Figure 2). Aqueous solutions of ammonium dihydrogen phosphate dissolved only ~10 % of the slags vanadium, but was more selective than above mentioned acids; only calcium (58-184 mg/l), magnesium (22-36 mg/l) and silica (242-358 mg/l) were dissolved from the slag in addition to vanadium (34-52 mg/l). Compared to ammonium dihydrogen phosphate, aqueous solution of ammonium sulfate dissolved less vanadium (only 22-24 mg/l), more calcium (782-1666 mg/l), but less silica (58-66 mg/l) and no other elements.

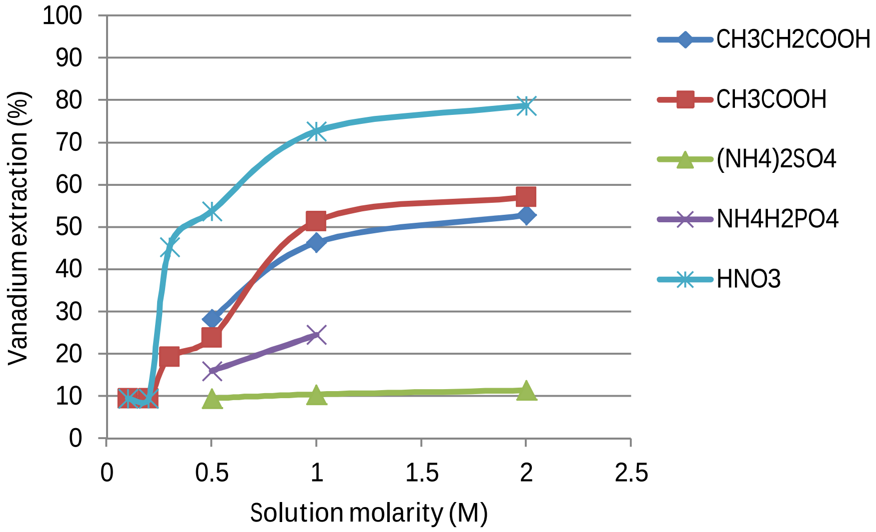

Figure 1. Dissolution of vanadium from steel converter slag (1 g) in aqueous solutions (50 ml) of HNO_3, CH_3CH_2COOH, CH_3COOH, $NH_4H_2PO_4$, and $(NH_4)_2SO_4$ at room temperature.

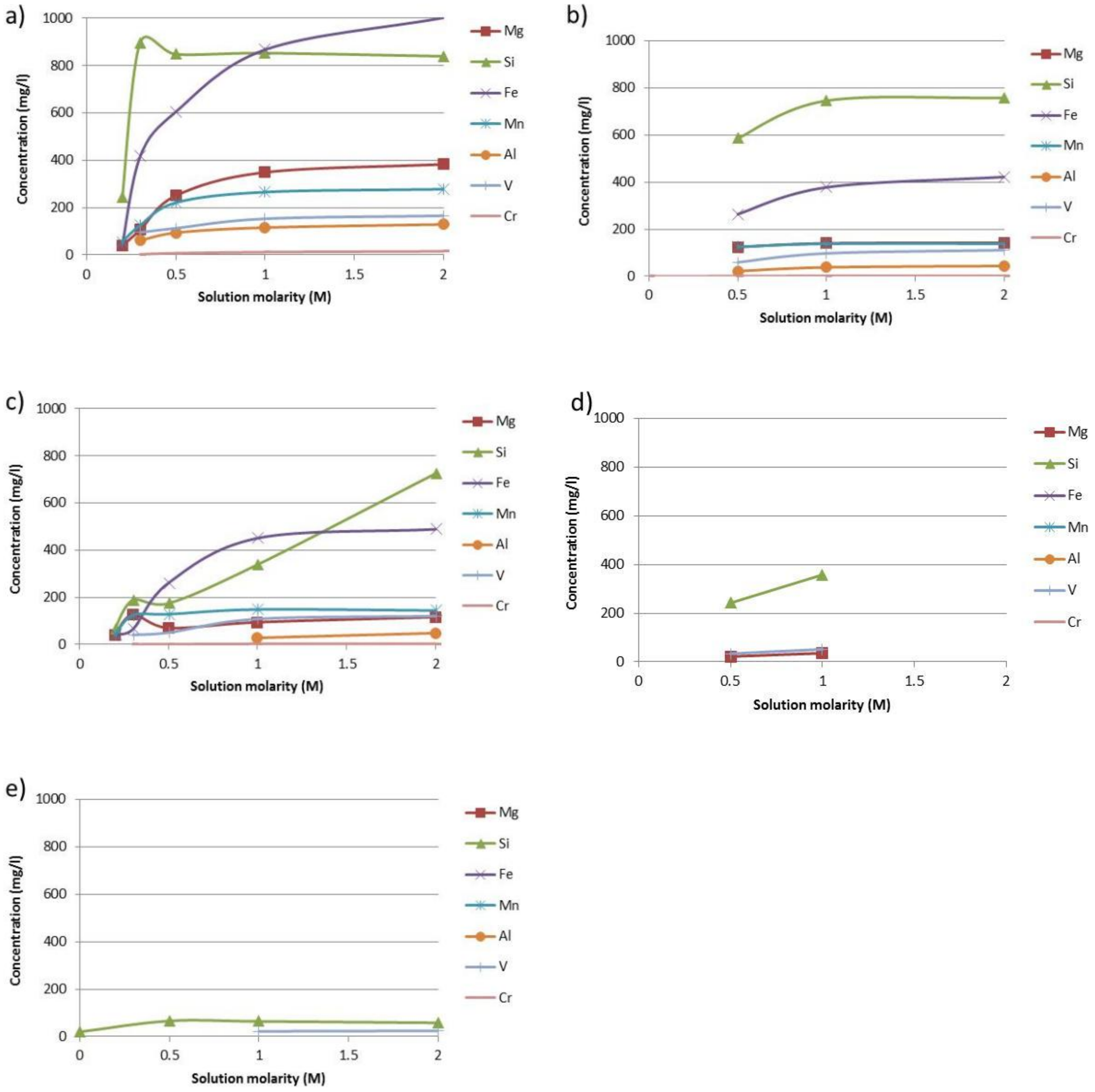

Figure 2 Concentration of measured elements (Mg, Si, Fe, Mn, Al, V and Cr) in aqueous solutions (50 ml) of a) HNO_3, b) CH_3CH_2COOH, c) CH_3COOH, d) $NH_4H_2PO_4$, e) $(NH_4)_2SO_4$ and steel converter slag (1 g). ! Concentration of calcium (up to ~6000 mg/l) is not shown in the pictures.

1.4 Dissolution of vanadium from residual slag-previous results reported in D514

In the previous report (D514), results concerning extraction of valuable metals from the residual slag of the Slag2PCC method were reported. Residual slag was obtained from the extraction reactor, where steel converter slag (from Ruukki) was mixed with an aqueous solution of ammonium salt (here: chloride). During the extraction step, part of the steel converter slag's calcium is extracted from the slag. Slag residue (called here "residual slag") was first washed with water, 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, prior to experiments made to investigate extraction of metals. The vanadium content of the steel converter slag used in these experiments (1.7 wt-% (XRF)) was slightly higher than that of the steel converter slag that was used in the experiments reported in section 1.3 (1.4 wt-% (XRF), 1.0 wt-% (ICP-AES)). A reason for this was that the slag with higher vanadium content was obtained from a batch were possible future steelmaking process changes at Ruukki in Raahe (giving a higher vanadium content in the slag) were simulated. It should be noted that in the experiments reported in D514, residual slag was used in the vanadium extraction experiments instead of the original steel converter slag. Vanadium content of this residual was 2.0 (wt-%, wet (ICP-AES)). None of the chosen solvents (sodium chloride, sodium hydroxide, ammonium sulfate or sodium bicarbonate) dissolved vanadium efficiently (Figure 3). Dissolution of vanadium (as percentage) in an aqueous solution of ammonium sulfate was in the same order of magnitude that in the experiments summarized in section 1.3 (where the same solvent was used). However, due to higher vanadium content of the residual slag, concentration of vanadium in the solution was higher (52-57 mg/l vs 22-24 mg/l).

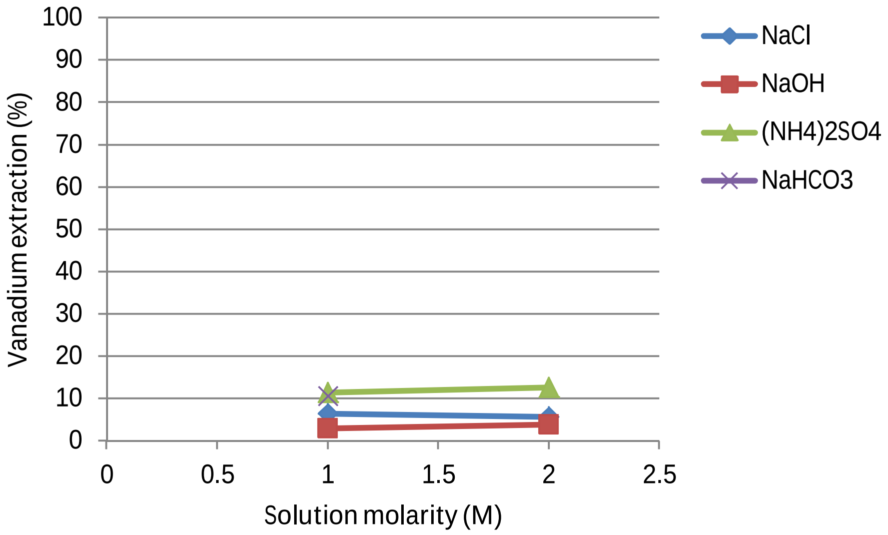

Figure 3 Dissolution of vanadium from residual slag (3 g) in aqueous solutions (150 ml) of NaCl, NaOH, $(NH_4)_2SO_4$ and $NaHCO_3$ at 30 °C.

1.5 Suggestions for the experimental work to be made

Regardless of acids (nitric acid, acetic acid and propionic acid) not being selective for extracting vanadium from steel converter slag, it is reasonable to test them on the residual slag, since they were able to dissolve considerable amount of the steel converter slag's vanadium. Since the highest tested concentration of aqueous solution of sulphuric acid was only 0.1 M, it would make sense to test that acid with residual slag using stronger solution, especially since the tests with sulphuric acid have been reported in the open literature concerning extraction of vanadium. Aqueous solution of ammonium dihydrogen phosphate could be tested as well, due to its higher selectivity for vanadium.

Solution strength of 0.5 and 1 M could be used in the experiments where nitric acid, propionic acid and acetic acid are used, as in our earlier experiments (section 1.3) leaching of vanadium from steel converter slag was more significant from 0.5 to 1 M than from 1 M to 2 M. Similar solution strengths could be used also with sulphuric acid. Since the strongest solution strength tested with ammonium dihydrogen phosphate was 1 M, also 2 M solution could be tested in addition to 0.5 and 1 M solutions.

Aqueous solution of sodium sulphate could be tested as well, because of the finding of Tavakoli et al (2013) that sulphate concentration in solution increases solubility of vanadium. This solution should be pH-neutral and thus might not be able to dissolve vanadium from the residual slag by itself. Therefore, it could also be tested as an additive to another one of these solvents described above.

Based on the other findings of Tavakoli et al (2013), aqueous solution of sodium hydroxide at higher temperature could also be tested.

Although roasted material has been used in many of the experiments reported in the open scientific literature, roasting itself is likely too complicated and energy-intensive for the goals aimed at here.

2 Experiments

2.1 Methods

Residual slag used in the experiments was gathered from the extraction reactor of the pilot plant. Experimental conditions in the extraction reactor (from where the slag residue was filtered from) were following: 10 kg of steel converter slag from Ruukki (0-1000 µm), 150 l of aqueous solution of NH_4Cl (1M), 200 rpm, time 1 hour. Before gathering, the residual slag had been stored overnight under the solvent from the extraction reactor. After gathering, as much of the solvent as possible was filtered and the slag was stored in closed glass jar. Part of this slag (~100 g) was washed with distilled water (2*500 ml) and dried in the oven (at 125 °C for overnight). It was then calculated that untreated slag weights about 1.27 times more than the washed and dried slag. Untreated slag was used in these experiments, but both were analyzed with ICP-AES in order to be able to later compare the results if experiments are to be made with washed and dried slag.

Batches of 12.7 g of residual steel converter slag from the extraction reactor (in which calcium was dissolved from the slag) was dissolved in 500 ml aqueous solution of acetic acid (0.5 and 1 M), propionic acid (0.5 and 1M), sulphuric acid (0.5 and 1 M), nitric acid (0.5 and 1 M), sodium hydroxide (1 M) or ammonium dihydrogen phosphate (0.5, 1 and 2 M). The reason for choosing these solvents is explained in Section 1.5. Solution temperature was kept at 30 °C, except with sodium hydroxide, which had already been tested at that temperature (now 70 °C). Further, one additional experiment was made using aqueous solution of ammonium dihydrogen phosphate (1M) at 65 °C.

The solutions were stirred by a magnetic stirrer for an 1 hour. Solution samples of 10 ml were taken 5, 20, 40 and 60 minutes after addition of the slag. The solutions were immediately filtered and sent for analysis. The concentrations of V, Ca, Si, Fe, Al, Mn, Cr and Mg in the filtered solution samples were measured with Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). Currently, only the last sample of each test has been analyzed, the rest will be analyzed only if it seems reasonable.

2.2 Results

Selected solvents were able to dissolve 8-85 % of the slag residue’s vanadium within the 1 hour the experiments lasted (Figure 4). Sulphuric acid, nitric acid and 0.5 M solution of propionic acid were able to dissolve more than 50 % of residual slag’s vanadium. Despite of 0.5 M ammonium dihydrogen phosphate (which dissolved ~40 % of the vanadium), rest of the solvents dissolved 30 % or less of the slag residue’s vanadium. Interestingly, both propionic acid and ammonium dihydrogen phosphate dissolved more vanadium from the slag residue when 0.5 M solution was used instead of 1 (or 2) M solution.

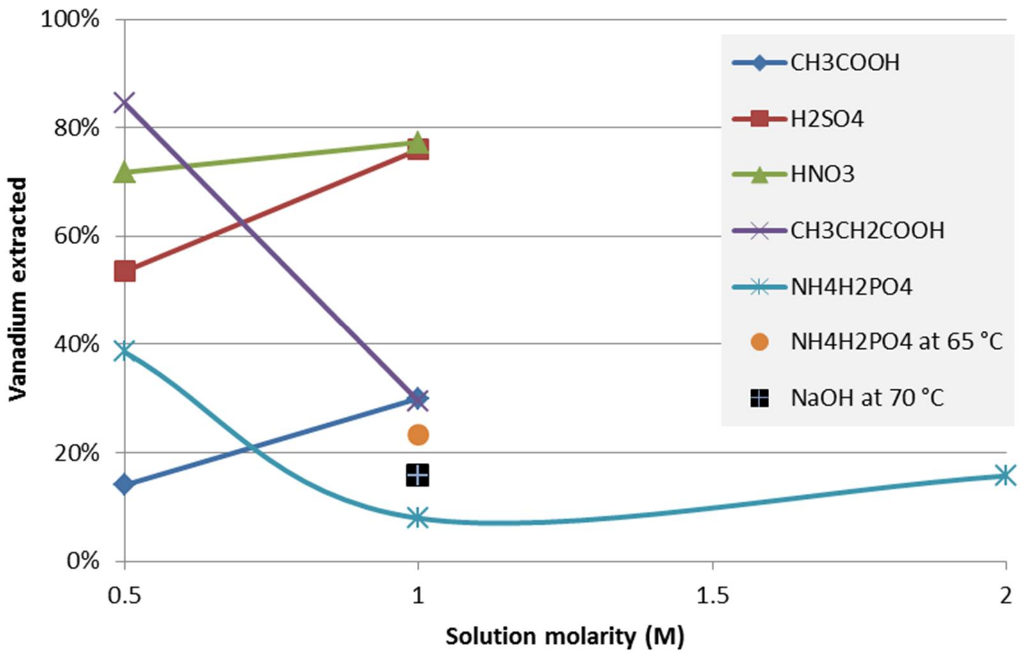

Figure 4. Dissolution of vanadium from the slag residue in aqueous solutions of selected solvents at 30°C.

Concentrations of the selected elements in the tested solvents are shown in Figure 5. As it can be seen, significant amount of calcium was dissolved in most of these solvents. It seems that for some reason (currently unknown), the conditions in the pilot had not been effective for extraction of calcium, thus it is more interesting to look at these figures so that calcium concentration has been excluded (Figure 6). From this, it can be seen that those solvents that dissolved 40 % or more of the vanadium, dissolved also other elements, mainly silica and/or iron.

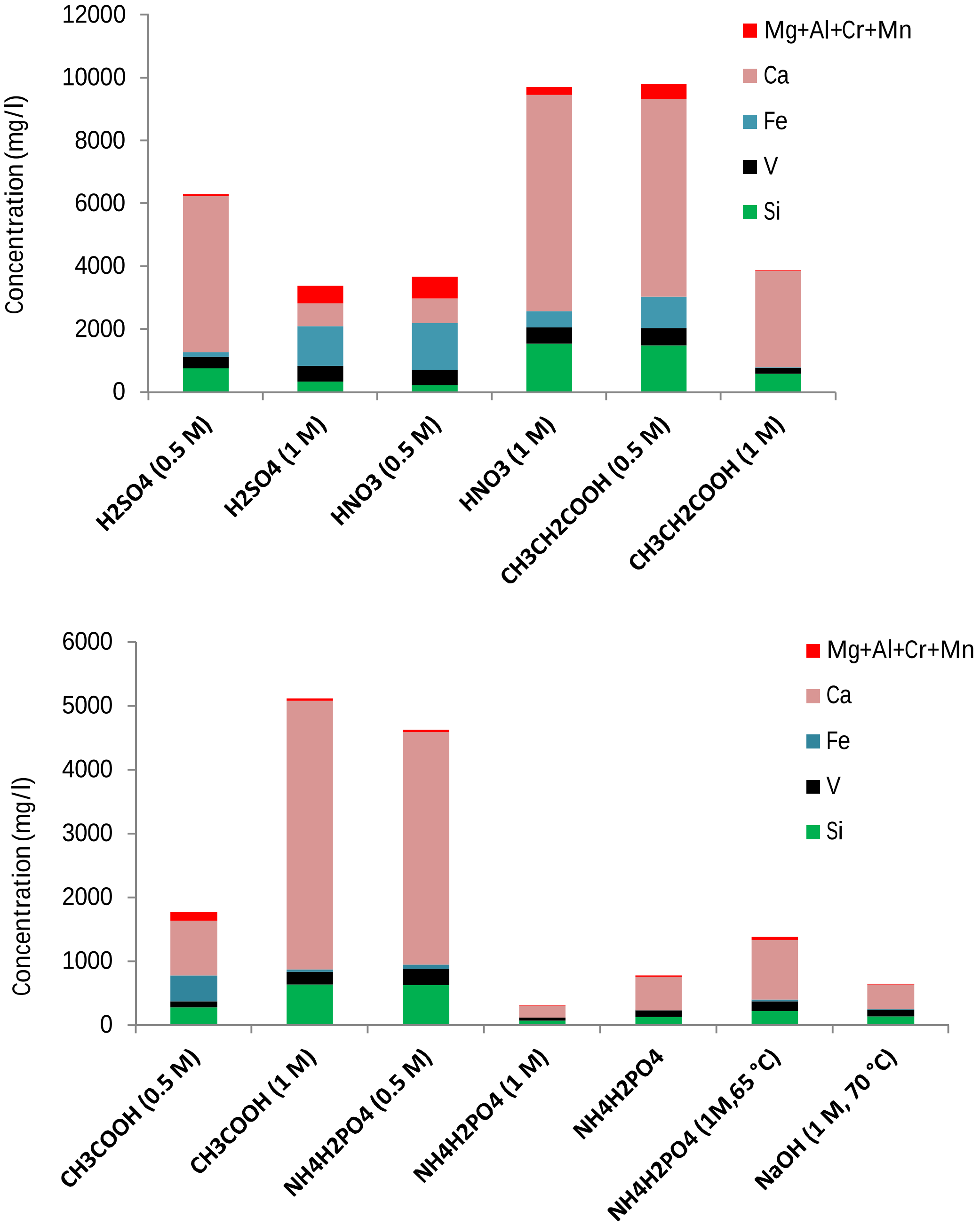

Figure 5 Dissolution of selected elements from the slag residue in aqueous solutions of various different solvents within an hour.

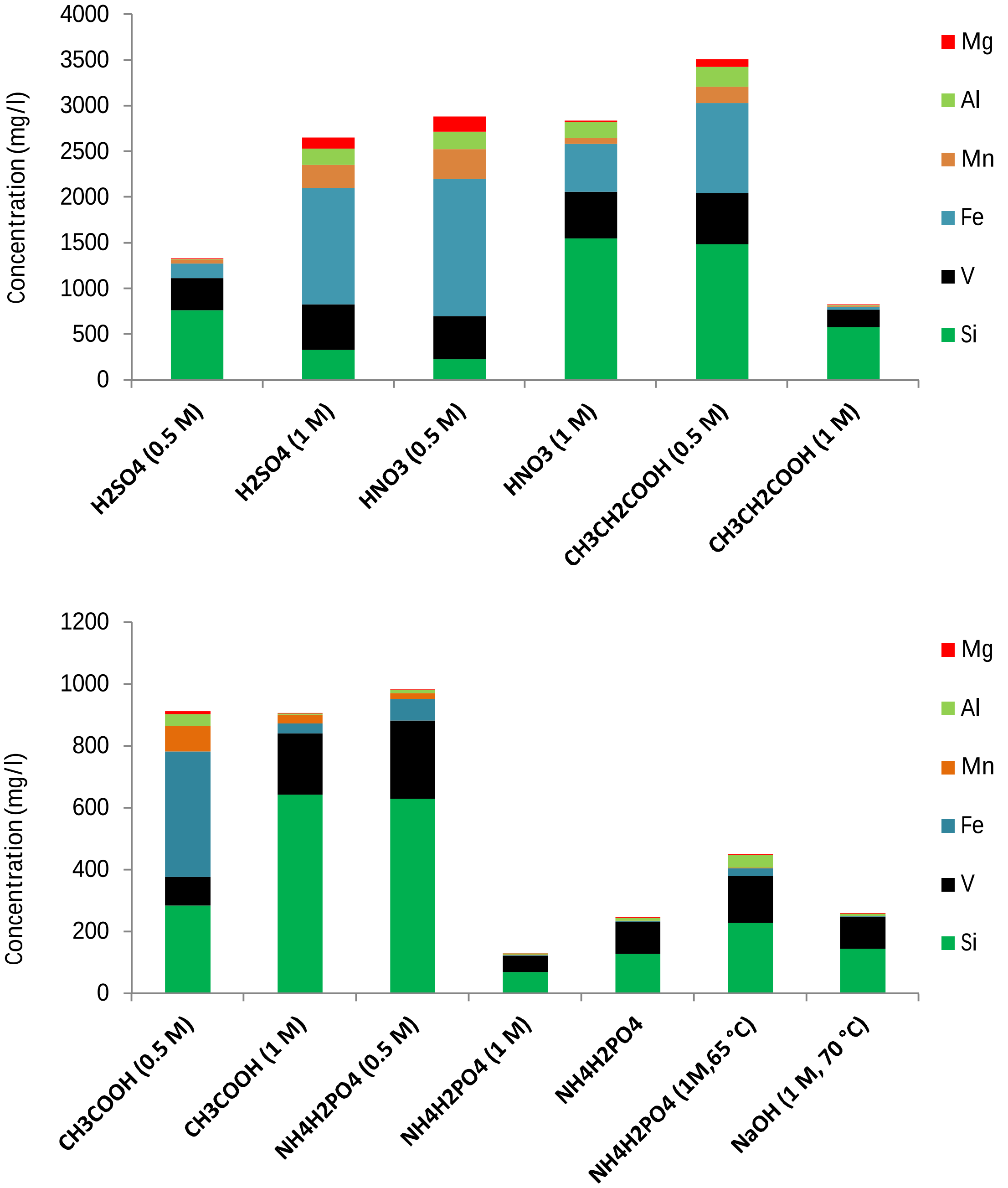

Figure 6 Dissolution of selected elements from the slag residue in aqueous solutions of various different solvents within an hour (calcium is excluded from this figure). (Note: also chromium is excluded, because it was detected only from 1 M H2SO4 and 0.5 M HNO3, and even then its concentration was less than 6 mg/l).

3 Conclusions

This report presents the current state of our research, in which the vanadium extraction from the residual slag of the Slag2PCC-method is investigated. Neither the literature review nor results from our earlier experiments indicated anything very interesting to be tested for. However, couple of different acids, ammonium dihydrogen phosphate and sodium hydroxide were chosen to be tested. While significant amount of the residual slag's vanadium was dissolved in sulphuric acid, nitric acid and 0.5 M solution of propionic acid, these were not selective for vanadium. In addition to calcium, which was dissolved in significant amounts (most likely because of the poor extraction conditions in the extraction reactor of the pilot), also other elements, mainly silica and/or iron were dissolved. Therefore, it can be concluded that none of the tested solvents are suitable for dissolving vanadium efficiently and selectively from the residual slag. However, if economic way can be found to recover vanadium selectively from these solutions, then these solvents might be useful.

4 References

Aarabi-Karasgani M., Rashchi F., Mostoufi N., Vahidi E., 2010. Leaching of vanadium from LD converter slag using sulphuric acid. Hydrometallurgy, 102, 14-21.

Polyak D. E., 2013. Vanadium (Advance release). USGS, 2012 Minerals Yearbook. Available at: http://minerals.usgs.gov/minerals/pubs/commodity/vanadium/ (Accessed January 9th, 2014)

Roskill, 2013. Webpage for ordering: Vanadium: Global Industry Markets and Outlook, 13th edition 2013. Available at: http://www.roskill.com/reports/steel-alloys/vanadium (Accessed January 9th, 2014)

Tavakoli M. R., Dornian S., Dreisinger D. B., 2013. The Leaching of Vanadium Pentoxide using Sulphuric Acid and Sulphite as a Reducing Agent. Accepted manuscript for Hydrometallurgy (2013), doi: 10.1016/j.hydromet.2013.10.014

Tveit T., Eloneva S., Said A., Fogelholm C.-J., Revitzer H., Zevenhoven R., Mattila H.-P., Forsman A.-M., Fält M., 2009. Reduction of CO_2 emissions and utilization of slag products by producing calcium-based products from carbonate-free slag products (Slag2PCC Plus), final report 1.1.2007-30.6.2009.

Van Zomeren A., van der Laan S.R., Kobesen H. B. A., Huijgen W.J.J., Comans R. N. J., 2011. Changes in mineralogical and leaching properties of converter steel slag resulting from accelerated carbonation at low CO2 pressure. Waste Management, 31, 2236-2244.

Xiao Q., Chen Y., Gao Y., Xu H., Zhang Y., 2010. Leaching of silica from vanadium-bearing steel slag in sodium hydroxide solution. Hydrometallurgy, 104, 216-221.

Ye G., 2006. Recovery of Vanadium from LD slag, A state of the art report, Part I – Facts and metallurgy of Vanadium. Jernkontorets forskning, stålkretsloppet, D 816, ISSN 0280-249X.

Ye G., Lindvall M., Magnusson M., 2013. Swerea Mefos perspective on metal recovery from slags. In Proceedings of the Third International Slag Valorisation Symposium, the transition to sustainable materials Management, March 19-20, 2013, Leuven, Belgium. Edited by Malfliet A., Jones P. T., Binnemans K., Cizer Ö., Fransaer J., Yan P., Pontikes Y., Guo M., Blanpain B.

Yang-ge Z., Guo-fan Z., Qi-ming F., Yi-ping L., Le-ming O., Si-jie H., 2010. Acid leaching of vanadium from roasted residue of stone coal. Transactions of Nonferrous Metals Society of China, 20, 107-111.