CHROMIC

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Use of ozone in leaching of metals

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Content

- Ozone applications
- Ozone in metallurgy and recycling...?
- Vanadium industrial importance - slags
- Practical example
    - Industrial waste processing: V leaching from slags (project Chromic)
- Challenges and conclusion

Ozone

High redox potential (+2,07 V)

Oxidize everything except glass, PTFE, stainless steel

Most effective at room temperature and lower

- Use: bleaching, waste waters purification, dentistry, cosmetics, disinfection
- Destruction: phenols, chlorinated organics, PCBs

- Prospective in ore treatment, hydrometallurgy and recycling due to its strong oxidation potential

Pilot tests: Gold mine, Xylem Water Solutions

- Pre- treatment by ozone; increased extraction from 53 to 85 % Au
- Cyanide destruction

$CN^- + O_3 \rightarrow CNO^- + O_2$ (170 gO_3/m^3)

- Reduction 99% CN, effluent output ---- 0.083 mg/l

Malysia, plant

Important and critical metals

2017 CRMs (27)			
Antimony	Fluorspar	LREEs	Phosphorus
Baryte	Gallium	Magnesium	Scandium
Beryllium	Germanium	Natural graphite	Silicon metal
Bismuth	Hafnium	Natural rubber	Tantalum
Borate	Helium	Niobium	Tungsten
Cobalt	HREEs	PGMs	Vanadium
Coking coal	Indium	Phosphate rock	

V – iron and steel metallurgy, human

Vanadis – Norse gooddes of beauty
V – acts as insulin (diabetes, cholesterol, heart disease, preventing cancer...
(red meat, fish, bean, apple, pear, plum, cabbage, garlic, blackberry, carrot, milk)

Vanadium

CRM list of 27 raw materials in EU (2017)
SET plan („Strategic Energy Technology Plan“) – support for development of low carbon technologies - 14 metals (Te, In, Sn, Hf, Ag, Dy, Ga, Nd, Cd, Ni, **Mo, V, Nb**, Se)

Vanadium –strategic metal for energy technology
Vanadium redox/flow batteries

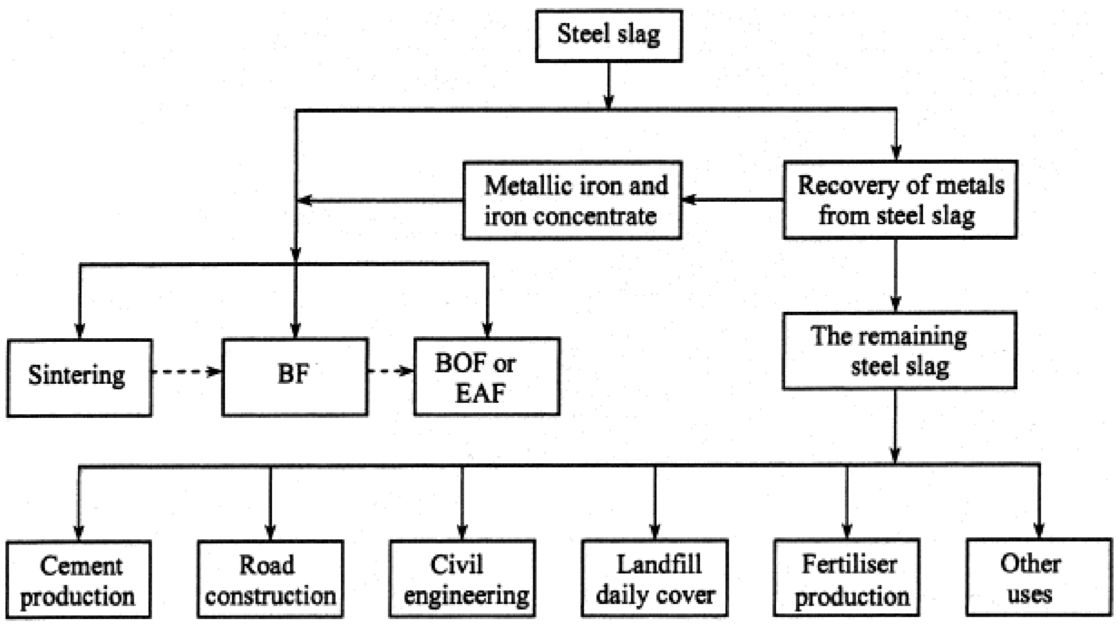
EU transition to a low carbon, resource efficiency ad circular economy
Importance of Recycling

V world production: 80 000 t/y
EU consumption: 12 000 t/y (no production)
more than 90 % need in metallurgy (steel)

Slag composition and utilization

- EAF slag (29 % of total slag generated), BOF slag (46%): majority of iron oxides
- Stainless steel, FeCr slags: low or no iron oxide, Ca, Si, Al, Mg
- Variety of metal content in alloyed steel and ferroalloys production
    - Cr, V, Ni, Mo, Nb, (Ti, Cu, Zn, REE...

- Vanadium - up to 6 % in high alloyed steel slags



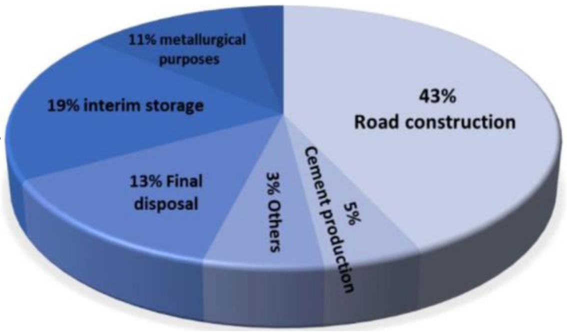
https://www.nzsteel.co.nz/products/aggregates/

Slag composition

Type of slag	SiO_2	Cr_2O_3	Al_2O_3	CaO	MgO	FeO	Fe_2O_3	Fe	V	Mn	Ti	Source
BOF	9-18	n	0,9-2,8	34-55	2,5-10	n	n	14-30	0,1-3	0,93-6,2	n	[15]
	9,31	0,20	2,20	41,59	8,93	22,4	n	n	0,5-1,22	2,7	1,092	[16]
LD	12-12,6	n	1,22-1,58	47,88-50,0	0,82-1,5	26,3-27,89	1,43-2,79	n	n	0,21	0,1-1,86	[10, 17]
	8,52	n	1,27	41,86	11,15	25,22	n	n	0,84-1,4	3,19	n	[18]
	17,6	0,56	0,52	23,8	5,85	n	n	17,3	1,65	7,1	2,50	[19]
EAF (carbon steel)	31,7	4,7	4.6	47.4	7.0	1,2	n	n	n	n	n	[10]
	25,6	2,00	10,6	31,6	11,9	14,5	n	n	0,028	2,43	0,48	[20]
EAF (high-alloy steel)	8,39	n	1	53,74	n	n	20,95	n	0,27-0,948	7,0	0,76	[21]
	17,6	0,56	0,52	23,8	5,85	n	n	17,3	5,88	7,1	2,50	[12]
Stainless steel	29,3-34,3	1,8-8,8	2,9-7,8	47,3-51,0	4,9-10,8	0,5-2,1	n	n	n	0,54-2,04	0,36-0,42	[22]
	26,5-33,5	2,39-2,84	1,65-10,07	43,27- 54,1	3,65-8,59	n	1,36-1,43	n	n	n	0,13-0,74	[23]
	29,36-40	3,67-4,00	4,13-4,5	36,7-46,6	4,59-5,00	0-9	6,13-6,5	n	n	n	n	[24]
	26,3-31,2	5,51-9,5	1,66-9,7	45,5-47,6	3,65-7,3	n	n	1,75-7,4	n	n	0,13-0,68	[15]
Ferrochrome	1	5	12	36	24	n	11	n	n	n	n	[15]
	26-30	14-16	22-24	2-3	24-26	2-4	n	n	n	n	n	[11]
	25-28	10-17	15-21	n	21-24	2-6	n	n	n	n	n	[25]
	42,10	6,04	5,86	0,95	10,30	3,98	n	n	n	0,26-0,5	0,08	[26]
	25-30	10-15	16-22	3-5	22-25	2-5	n	n	n	n	n	[27]
AOD slag	24,67	0,51	1,07	55,9	5,85	1,15	n	n	0,008	n	0,41	[14]

n – not analyzed; BOF – Basic Oxygen Furnace; EAF – Electric Arc Furnace; LD – Linz-Donawitz (Oxygen Converter); AOD – Argon Oxygen Decarburization

Recovery of metals from slags



http://www.euroslag.com/PRODUCTS/ STATISTICS/2012

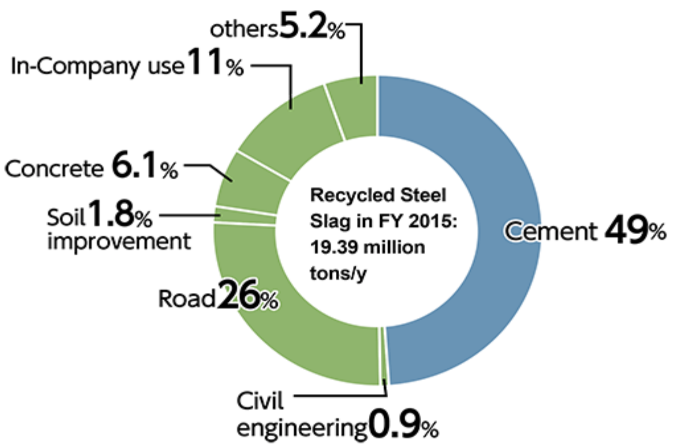
World situation: ~ 65 % recycled, 35 % landfilled

China: 22% recycled

EU situation: some countries more than 90 % usage

13 + 19 % disposal (final + internal storage

Problems in complex utilization – some slag



NSSMC's Use of Recycled Steel Slag

-Future application: majority for cement industry

- The industrial scale processes for recycling of slags (FeCr, FeV, SS, EAF...) for metals recovery - still missing

- Limitation as a construction material: due to some heavy metal content - Cr, Ni, V

- Ecotoxicity (leachable Cr(VI), V...

Slag recycling research

Direct application

Cement/Concrete

Asphalt mixtures

Phosphorous removal from melt

Hg removal from sea water

P/NH_4/As/Cu removal from WW

CO_2 sequestration (with NH_4Cl)

Desulphurization of gases (agglomeration process)

Amendment of soils

Agriculture

Metals recovery

Chromium
Vanadium
????????

Mechanically

- Magnetic separation;
- Gravity separation
- Senzors
- Sieving

Hydrometallurgy

- Alkaline leaching
- Roasting/leaching

Pyrometallurgy

- Reduction by Si, Al, C, SiC

New materials recovery

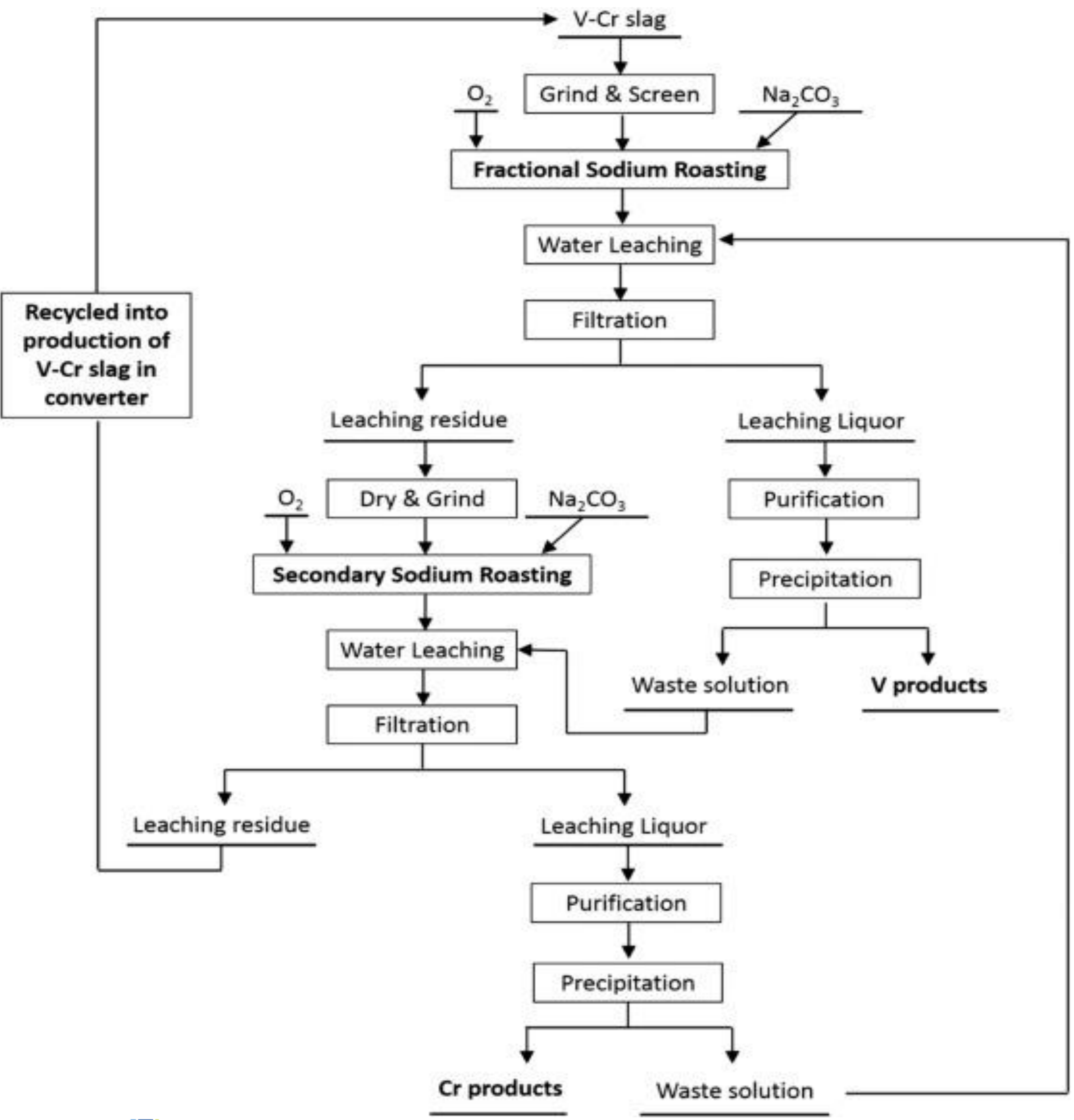
Ceramic composite

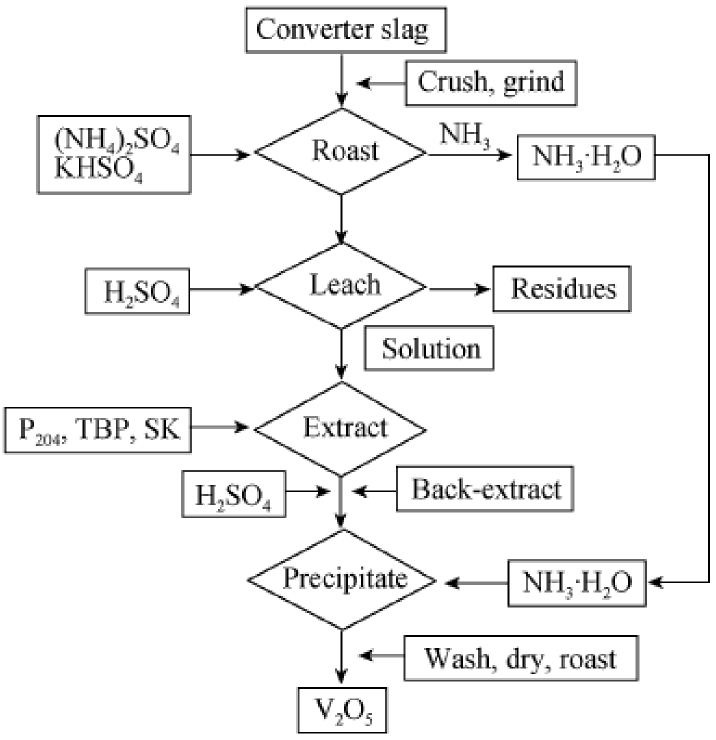
Refractory concrete

Glass-ceramics

Composite coagulants

Possible combined method for Cr/V recovery from slag





EXPERIMENTAL

- **Ozonation leaching - for possible V recovery from slags**
  - **Slag samples characterization (CHROMIC)**
  - **Ozonation leaching of slags (alkaline)**
  - **Focusing on Vanadium recovery**

Project CHROMIC

The aim

- to develop new processes for effective treatment of various industrial wastes (slags) in order to recover chromium, vanadium and other valuable metals (niobium, molybdenum).

- “Releasing” Cr, V, Nb, Mo from mineral structures and slag matrix and selectively recover choosen metals
- to obtain the products, suitable as the construction materials.

<u>Method applied: Hydrometallurgy</u>

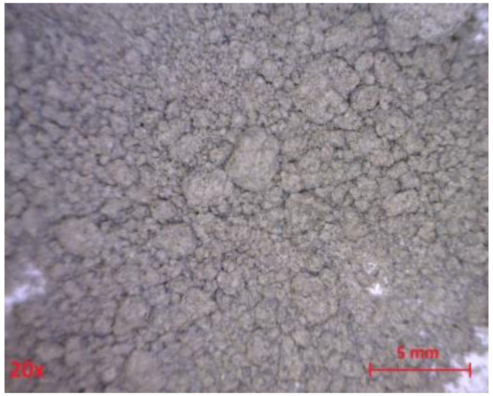
The slags used for investigation:

1. **CHR1 EAF slag**
2. **CHR2 Slag from FeCr production**
3. **CHR3 Slag from stainless steel**

Photo: Getty Images, http://uk.businessinsider.com

Materials and methods

Experimental samples supported by Chromic partners



CHR1 – EAF slag

3.9891 g/cm³

Magnetic

CHR2 - FeCr slag

3.2741 g/cm³

Non-magnetic

CHR3 – stainless steel slag

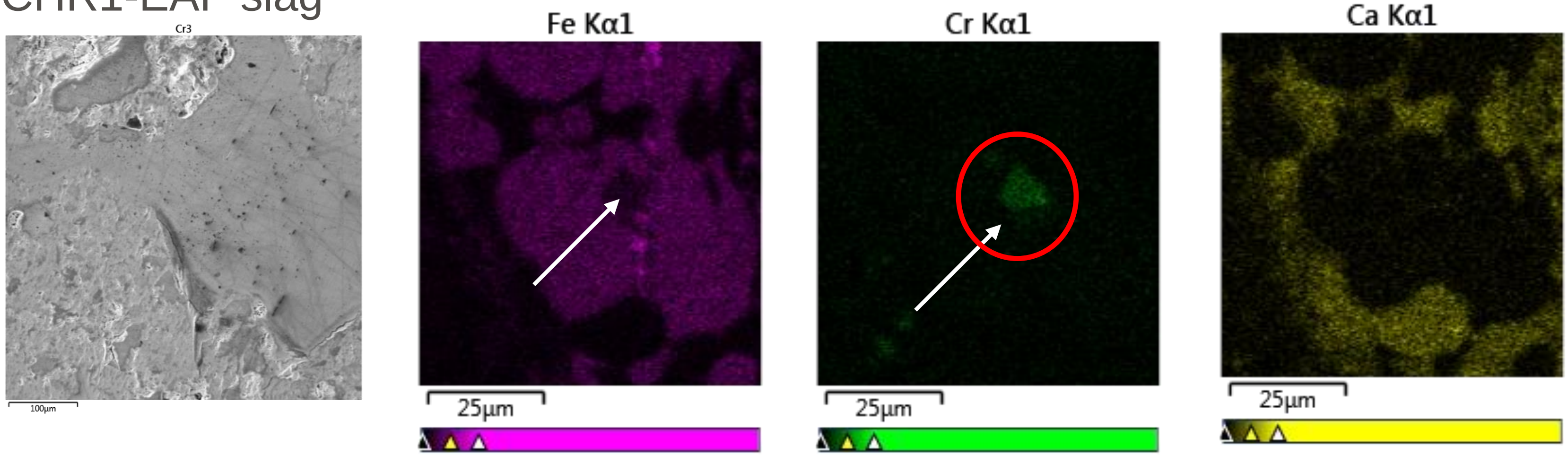
3.0753 g/cm³

Partially magnetic (around 14 %)

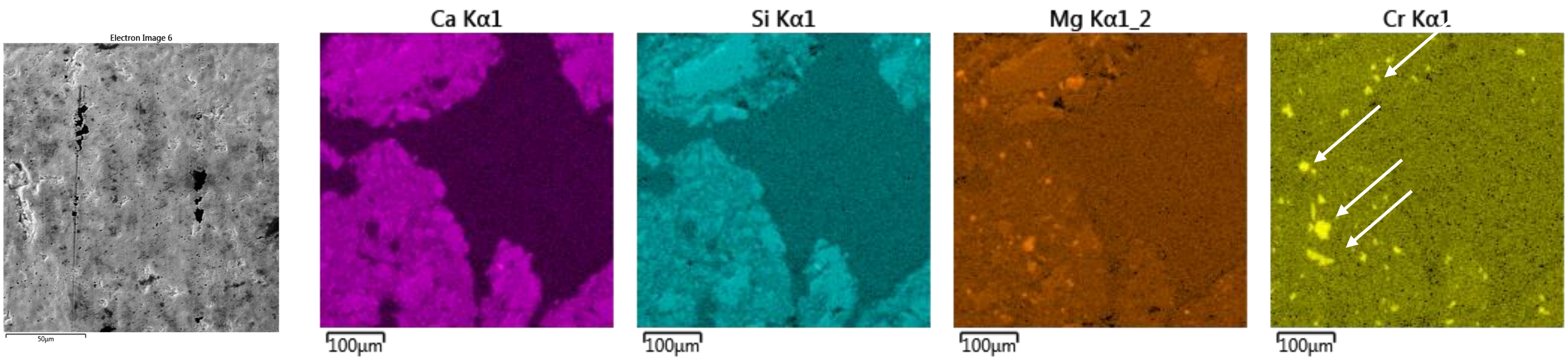
Slags microstructure

SEM pictures - Isolated particles with Cr content

CHR1-EAF slag



CHR3 – SS slag



Ca a Si together - $2CaO.SiO_2$, MgO, Cr localized (or with Mg - $MgCr_2O_4$), FeMnCr

Elemental composition

Chemical analysis

	Cr	V	Fe	Mg	Ca	Al	Si
CHR1	2.85	0.0717	31.82	1.4	17.37	4.24	4.54
CHR2	3.64	0.016	0.428	3.89	31.9	2.29	13.49
CHR3	2.22	0.0493	0.68	2.66	30.62	1.19	11.58

Mineralogical composition

EAF slag

- FeO, gehlenite, Ca_2SiO_4,
- magnetite/magnesioferrite
- $FeCr_2O_4$ (chromite)
- $CaCO_3$, calcium aluminate

FeCr slag

$2CaO.SiO_2$, $3CaO.SiO_2$,
Mg componds (MgO, spinel)
Cr - in complex spinel (magnesiochromite, spinel)
- $CrPO_4*6H_2O$, Ca_2FeNbO_6 ?

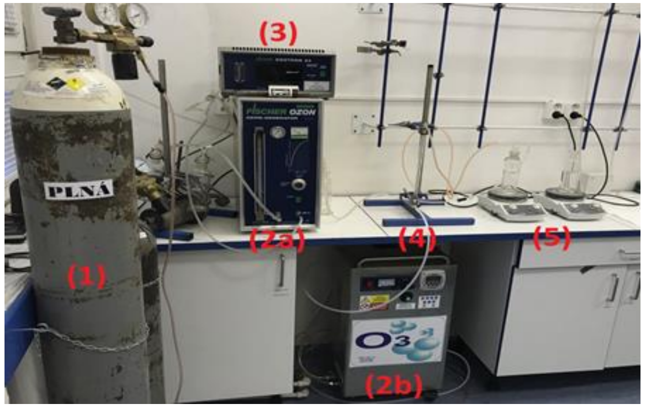
-Ni2FeVO6 ?

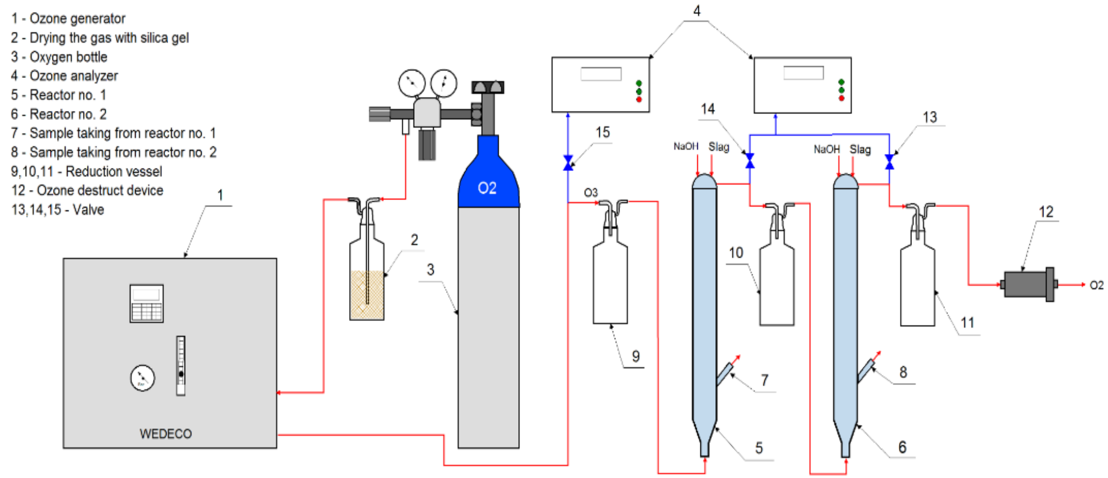
SS slag

merwinite, $2CaO.SiO_2$, gehlenite
$CaCO_3$, $Ca_4Si_2O_7F_2$ (cuspidine)
γ-Fe_2O_3 – maghemite
$CaMn(P_2O_7)$
$Ca_4Al_6CrO_{16}$, $NaK_3(CrO_4)_2$, doped in akermanite

Methodics - Slags leaching

- Ground and sieved samples – used fraction 90-125 µm





Experimental setup:

a) pilot ozonation leaching apparatus - with low ozone rates (8 g/hr); *1) pressure cylinder (O_2), 2) ozone generators3) ozone analyzer, 4) flow rate meter and 5) reaction vessel*

b) New ozonation apparatus (higher ozone rates 84.2 g/hr):

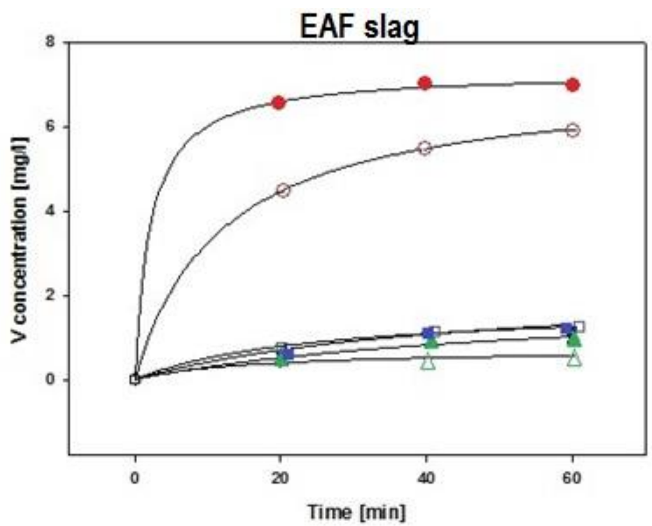
Experimental conditions:

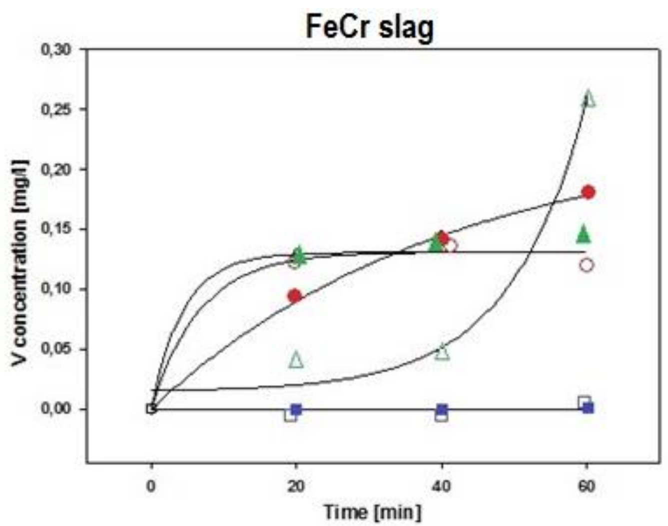
- *Old apparatus arrangement*: 10 grams of slag sample leached in 200 ml of solutions
- gaseous ozone bubbled through the frit (gas flowrate 250 l/hr, 33,5 g.m^3 O_3, 8 g/hr O_3)
- 2M solutions of NaOH, Na_2CO_3, KOH were used – studied three slags EAF (low carbon), FeCr, stainless steel slag)
- *New apparatus arrangement:* 25 g of slag, 500 ml of solution (gas flowrate 325 l/hr, up to 84.2 g/hr O_3) – NaOH, KOH, Na_2CO_3, NH_4OH, sodium oxalate and oxalic acid - only EAF slag tested

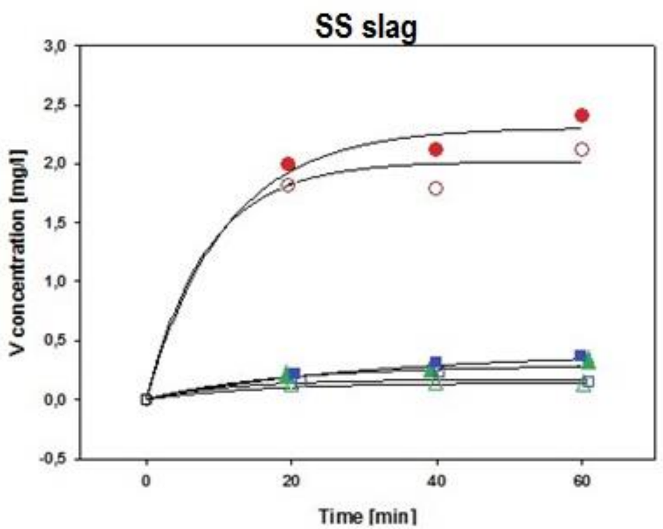
RESULTS: Ozonation leaching of V – low ozone flow rate

Vanadium leaching – pilot tests with low ozone flow rates (up to 8 g/hr O_3)

V – leached up to 18 % in ozonation leaching



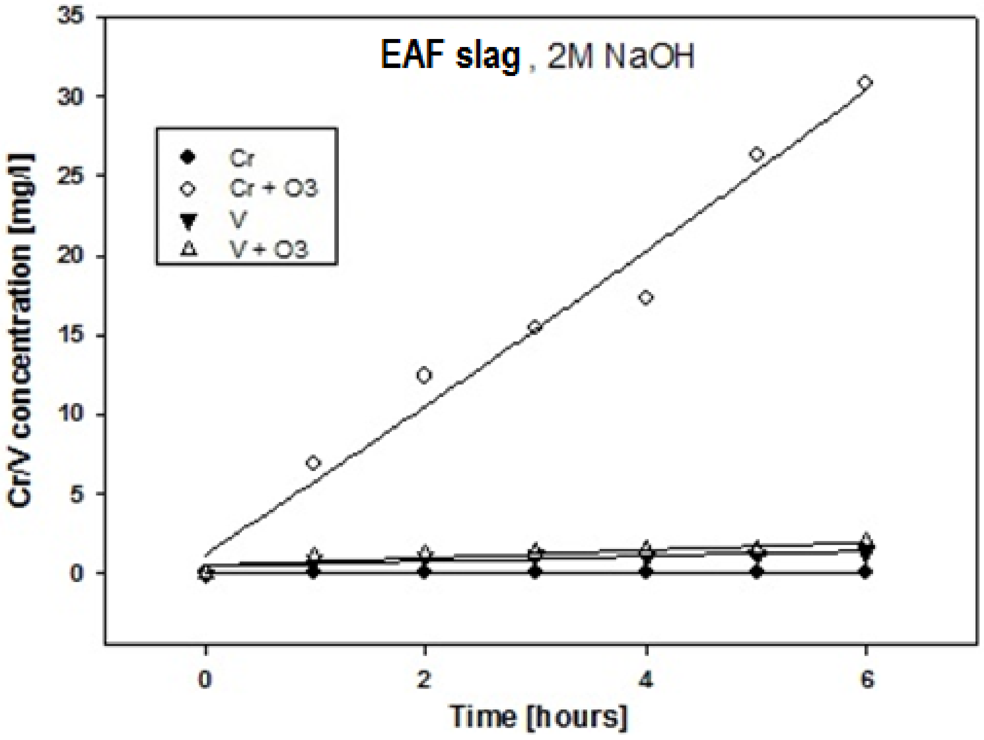




2M Solution, 200 ml, 10 g sample, ambient temperature, 500 RPM
O_3: 250 l/hod, 33,5g/m^3

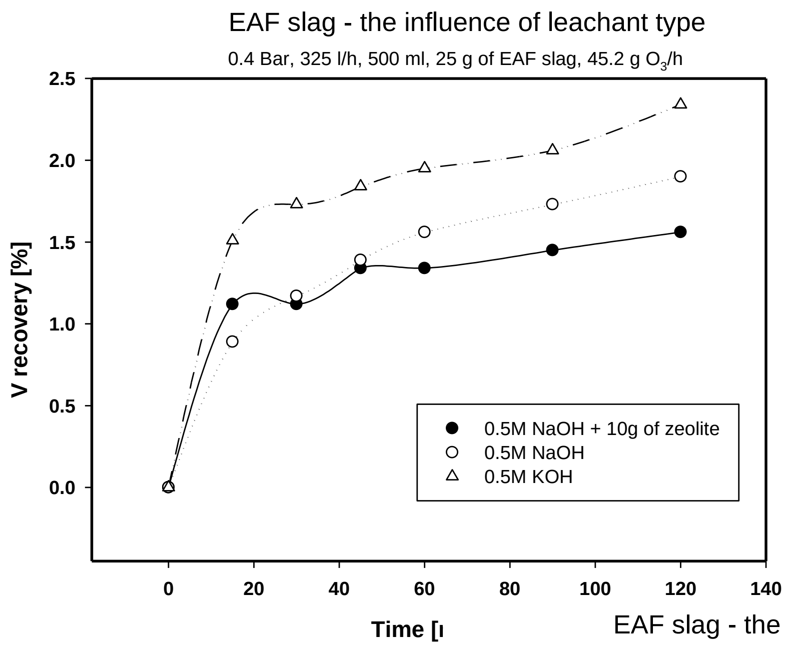
	Na_2CO_3	NaOH	KOH
Without O_3	○	△	□
With O_3	●	▲	■

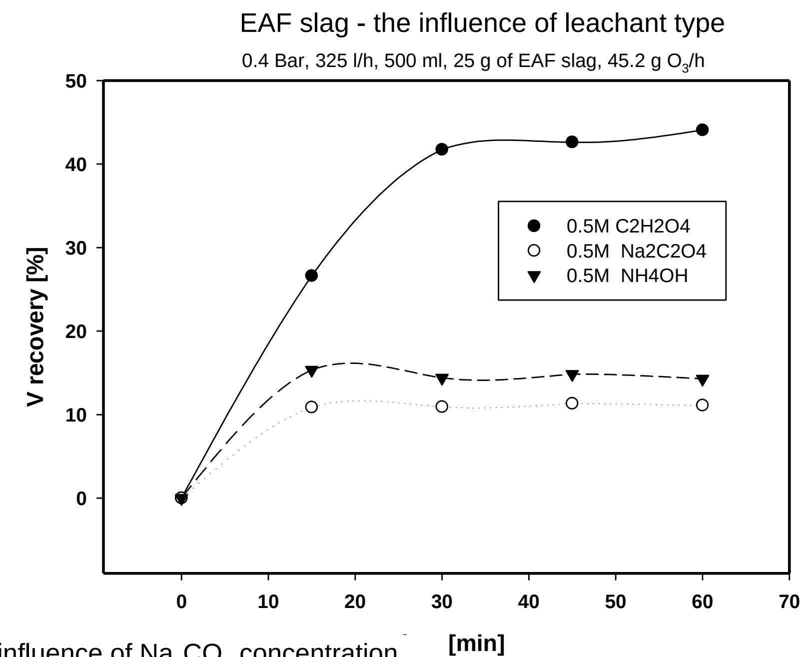
Long-period ozone leaching of EAF slag (8 g/hr O_3)

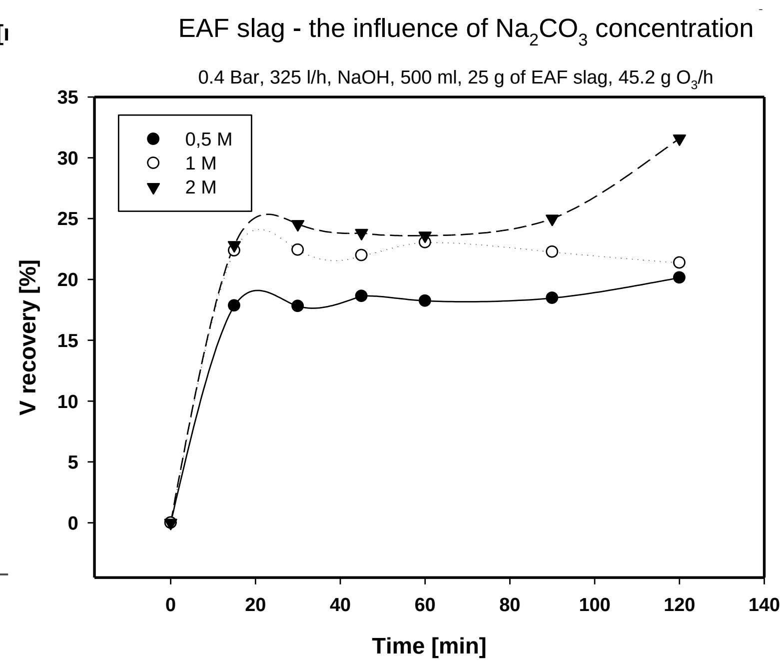


RESULTS: Ozonation leaching of V – high ozone flow rate

Vanadium leaching – pilot tests with high ozone flow rates (up to 84 g/hr O_3)







Conclusions and challenges

- Some slags with higher V and other important metals – suitable source of metals to be recovered
- Not yet industrially proven technology for recovery metals from slags: Cr, V, Mo, Nb
- Problems to release V (also Cr) from stable matrix
- IRT (FMMR, TUKE) – testing the ozonation leaching processes for metals recovery from slags
- Laboratory testing of slag leaching
    - In NaOH, KOH media – low efficiency for V leaching, FeCr and SS slags are inert
    - Ozone enhance the leaching proces of V from EAF slag in NaOH – but still too low
    - Helpful: Prolongation of leaching period
    - The best leachibility of V from EAF slag in Na_2CO_3 solution at higher ozone flow rates
    - Prospective – oxalic acid, too, but leaching of matrix in higher extent!
    - Other possibilities for improving the leachability of V using ozone (Cr) are still under investigation

- **Potential options for improved ozonation leaching of slags:**
    - Conditions of leaching (more effective solubilisation of ozone)
    - Combination of leaching agents, a proper concetration adjusting
    - Special pretreatment of samples
        - mechanical activation of slags
        - roasting without or with additives and leaching by ozone

Thank you for your attention!

www.chromic.eu