EASES

European Academic Symposium on EAF Steelmaking

IOB Department for Industrial Furnaces and Heat Engineering | RWTH AACHEN UNIVERSITY

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workshop on the "(re)use of primary and secondary raw material fines in the EAF

Influence of raw-material fines recirculation in EAF on slag quality

RFCS Fines2EAF project

POLITECNICO MILANO 1863

DIPARTIMENTO DI MECCANICA

INTRODUCTION

the **Fines2EAF** project aims to increase the value of steelmaking residues by internal recycling and (re)use in the form of cement-free bricks

this leads to several advantages

- ↘ avoid disposal of wastes
- ↘ enhance the use of primary raw material fines
- ↘ recycling of secondary raw material fines for steel production
- ↘ save costs
- ↘ reduce the environmental impact of the steel plant on the surrounding

sustainability of the project is given only if

- ↘ steel quality is not affected by fines recirculation
- ↘ **slag quality is not affected by fine recirculation**

investigation on the influence of bricks use on slag quality is fundamental

EXPERIMENTAL PROCEDURE – BRIQUETTES DETAILS

several samples were supplied by industrial partners

- Sidenor → 4 samples
- MarienHuette → 9 samples
- Lech Stahlwerke (MAU) → 29 samples

different types of bricks were used

- self-reducing (CC, MA) → tested in Sidenor
- slag former (MH, MI) → tested in MarienHuette & MAU

Recipe	Binder	oxycutting fines [%]	combustion chamber dust [%]	grinding sludges [%]	carbon powder [%]	binder [%]	water [%]
CC	sugarcane molasses	40.9	40.9		15.25	3.0	< 3
MA	polymeric	34.5	-	46.5	13.40	1.4	4.2

Recipe	Binder	ladle slag [%]	spent refractories [%]	starch [%]	fibers [%]	water [%]
MH 31 R/6	wheat starch	88.6	-	5.3	0.9	5.3
MH 31 R/4	wheat starch	91.7	-	3.7	0.9	3.7
MH 52 B	potato starch	69.3	20.8	3.6	0.9	5.4
MH 52 B/4	potato starch	46.4	46.2	3.6	0.9	2.9
MI 31 R	wheat starch	53.1	38.5	7.7	0.77	9.9
MI 52 C	potato+wheat	53.4	38.7	7.8	0.2	10.1

EXPERIMENTAL PROCEDURE – CHARGING PROFILE

Sidenor

↘ 1° trial

# of heats	Brick recipe	Charged materials	Sample codename
3	-	standard procedure	S 1
3	CC	5000 kg briquettes	B 1

↘ 2° trial

# of heats	Brick recipe	Charged materials	Sample codename
3	-	standard procedure	S 2
3	MA	5000 kg briquettes	B 2

EXPERIMENTAL PROCEDURE – CHARGING PROFILE

MarienHuette

↘ 1° trial

# of heats	Brick recipe	Charged materials	Sample codename
3	-	900 kg lime + 300 kg dolo lime	Reference
3	MH 31 R/6	additional 500 kg briquettes	274036
3	MH 31 R/6	1000 kg briquettes (replacement dololime)	274104
3	MH 31 R/4	500 kg briquettes (partial replacement lime ~ 200 kg)	274181
4	MH 31 R/4	500 kg briquettes (partial replacement lime ~ 100 kg + dololime ~ 50 kg	274280

↘ 2° trial

# of heats	Brick recipe	Charged materials	Sample codename
3	MH 52 B/4	500 kg briquettes partial replacement lime ~ 200 kg)	275475
1	MH 52 B	500 kg briquettes (partial replacement lime ~ 100 kg + dololime ~ 50 kg)	275622
3	MH 52 B	531 kg briquettes (replacement dololime)	275809
1	MH 52 B	1000 kg briquettes (replacement dololime)	275810

Experimental procedure – charging profile

Max Aicher Umwelt

↘ 1° trial

# of heats	Brick recipe	EAF	Charged materials	Sample codename
2	MI 31 R/1	1	1000 kg dolomitic lime + 0 briquettes	MAU-R
4	MI 31 R/1	1	1000 kg dolomitic lime + 500 kg briquettes	MAU-1000-500
4	MI 31 R/1	1	800 kg dolomitic lime + 500 kg briquettes	MAU-800-500
4	MI 31 R/1	1	500 kg dolomitic lime + 500 kg briquettes	MAU-500-500
3	MI 31 R/1	1	0 kg dolomitic lime + 2.000 kg briquettes	MAU-0-2000

↘ 2° trial

# of heats	Brick recipe	EAF	Charged materials	Sample type
2	MI 52C	1	1000 kg dolomitic lime + 0 briquettes	MAU-E3-R
4	MI 52C	1	0 kg dolomitic lime + 2000 kg briquettes	MAU-E3-0-2000
2	MI 31 R/2	3	1000 kg dolomitic lime + 0 briquettes	MAU-E1-R
4	MI 31 R/2	3	0 kg dolomitic lime + 2000 kg briquettes	MAU-E1-0-2000

EXPERIMENTAL PROCEDURE – CHARACTERIZATION

slag samples were prepared by planetary ball milling

- 5 min intervals
- 250 rpm rotating speed
- 0.1 l zirconia grinding jar
- 100 g total zirconia ball mass

and characterized by XRD

- θ–θ Bragg-Brentano configuration 5 to 90 ° 2θ @ 1 °/min, 0.02 ° step size
- Cu Ka radiation (λ = 1.54 Å)
- 30 rpm rotating sample stage
- 1D D/teX Ultra 250 detector with XRF suppressor filter

and SEM

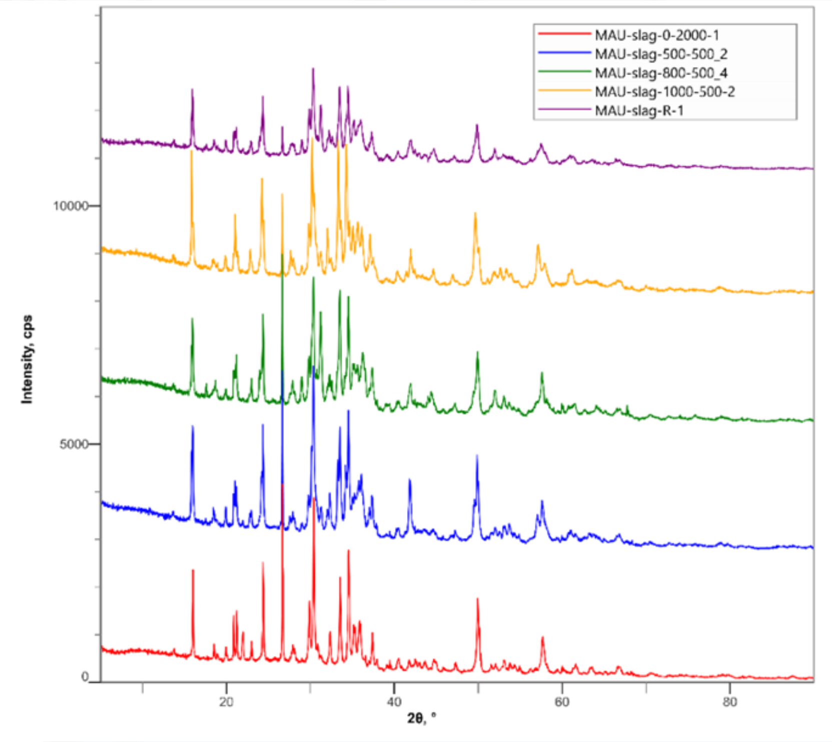
- slag fragment, molded in araldite-base resin and polished
- SEM-BSE analysis coupled with EDS

Leaching behaviour was investigate according to EN 12457-4:2002

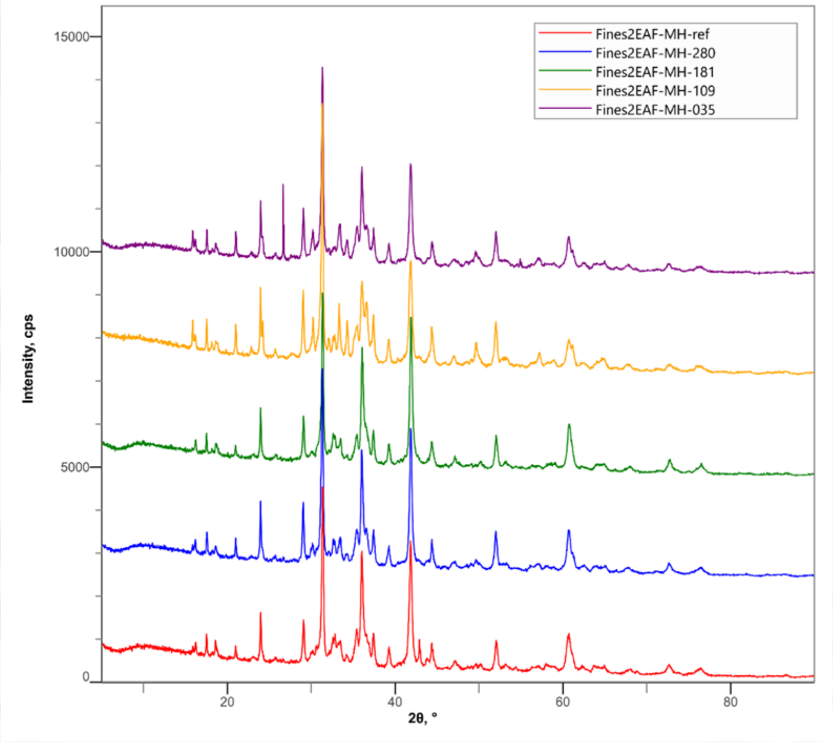
- no finely ground material *0.063mm<d<10mm*
- vacuum filtration *0.45 µm membrane filter*
- ICP-OES

RESULTS - XRD

- no differences in crystallographic composition
- within the intrinsic heterogeineity of the slag
- indipendent from type and amount of briquettes



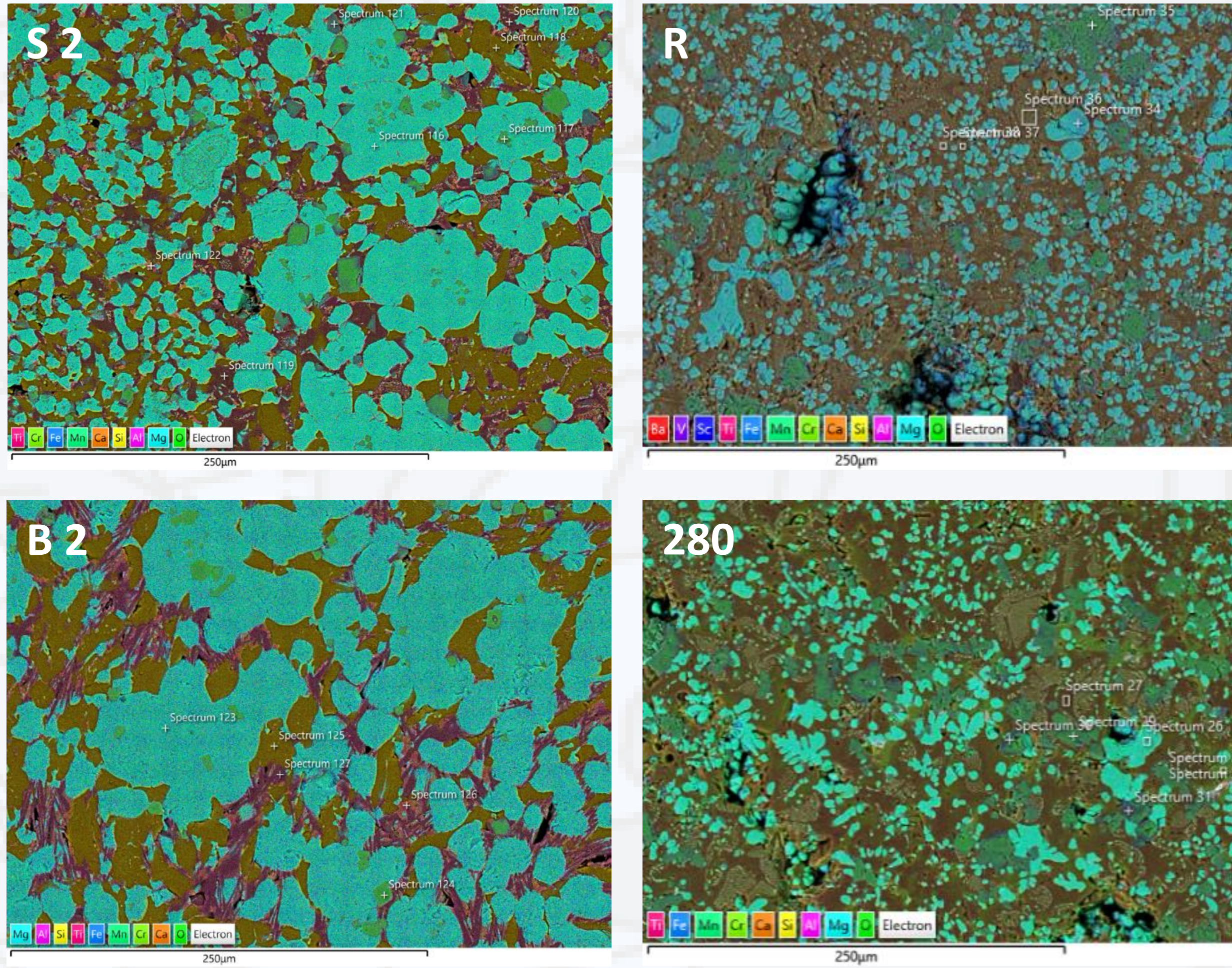
Max Aicher Umwelt



MarienHuette

Results - SEM

- no differences in morphologic and chemical characteristics
- within the intrinsic heterogeneity of the slag
- indipendent from type and amount of briquettes



Sidenor MarienHuette

Results – leaching test

Sidenor

Parameter	Unit	Limits*			1st trial		2nd trial	
		Type 1	Type 2	Type 3	S 1	B 1	S 2	B 2
Anions								
Cl	mg / kg	N/A	800	5	34	34	27.7	27.8
F	mg / kg	N/A	18	30	9.4	10.8	12.1	11.6
SO_4	mg / kg	N/A	1	5	183	159	99	87
Metals								
Sb	mg / kg	N/A	0.06	0.08	<0.5	<0.5	<0.5	<0.5
As	mg / kg	N/A	0.5	0.6	<0.5	<0.5	<0.5	<0.5
Ba	mg / kg	N/A	20	25	5.8	2	1.2	1
Cd	mg / kg	N/A	0.04	0.05	<0.4	<0.4	<0.5	<0.5
Cr	mg / kg	N/A	0.5	2	<0.5	<0.5	2.6	0.7
Cr (VI)	mg / kg	N/A	0.1	0.4	<0.5	<0.5	<0.3	<0.3
Cu	mg / kg	N/A	2	3	0.2	0.2	<0.5	<0.5
Hg	mg / kg	N/A	0.01	0.01	<0.1	<0.1	<0.5	<0.5
Mo	mg / kg	N/A	0.5	2.8	1.5	0.9	0.5	<0.5
Ni	mg / kg	N/A	0.4	0.5	<0.2	<0.2	<0.5	<0.5
Pb	mg / kg	N/A	0.5	0.6	<0.5	<0.5	<0.5	<0.5
Se	mg / kg	N/A	0.1	0.4	<0.5	<0.5	<0.5	<0.5
Zn	mg / kg	N/A	4	5	<0.2	<0.2	<0.5	<0.5
V	mg / kg	N/A	1.5	4	<0.5	1.9	1.3	1.4
Physical								
pH		N/A	N/A	N/A	11.67	11.19	11.61	11.52
EC	µS/cm	N/A	N/A	N/A	1106	337	755	594

* Type 1: bound application; Type 2: Unbound applications without complete impermeability coverage; Type 3: Unbound applications with complete impermeability coverage

RESULTS – LEACHING TEST

MarienHuette

Parameter	Electrical conductivity	pH	Ba	Cd	Cr tot	Co	Mo	Tl	V	W	F
Unit	µS/cm	-	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Limits	-	to 12.5	20.00	0.04	0.30	1.00	0.50	0.10	1.00	1.50	10.00
Reference	445	11.28	13.80	<0.4	<0.5	<0.5	0.50	<0.5	1.40	1.80	10.00
1st trial											
274036	293	11.08	7.10	<0.4	<0.5	<0.5	0.50	<0.5	0.90	2.30	10.70
274104	353	11.14	11.20	<0.4	<0.5	<0.5	0.30	<0.5	0.50	3.00	10.80
274181	426	11.36	7.30	<0.4	<0.5	<0.5	<0.5	<0.5	0.80	1.10	9.80
274280	399	11.26	7.70	<0.4	<0.5	<0.5	0.60	<0.5	1.00	3.70	10.60
2nd trial											
275475	542	11.40	6.20	<0.5	0.60	<0.5	0.60	<0.5	1.10	3.60	11.70
275622	642	11.50	7.20	<0.5	<0.5	<0.5	0.70	<0.5	1.60	2.50	11.10
275809	420	11.34	6.70	<0.5	<0.5	<0.5	<0.5	<0.5	1.30	1.40	12.20
275810	409	11.31	4.80	<0.5	<0.5	<0.5	<0.5	<0.5	1.30	1.40	11.60

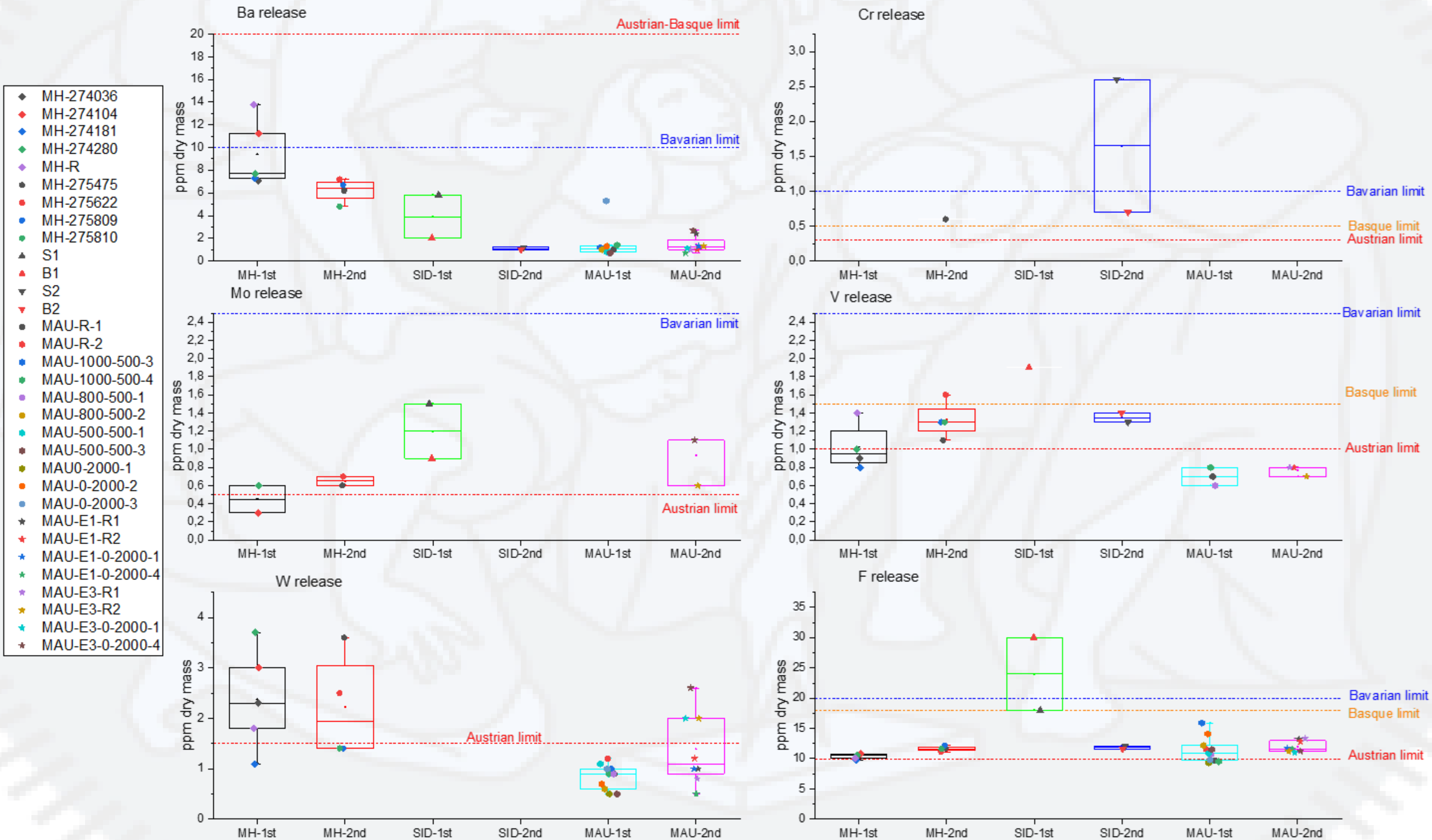
RESULTS – LEACHING TEST

MaxAicherUmwelt

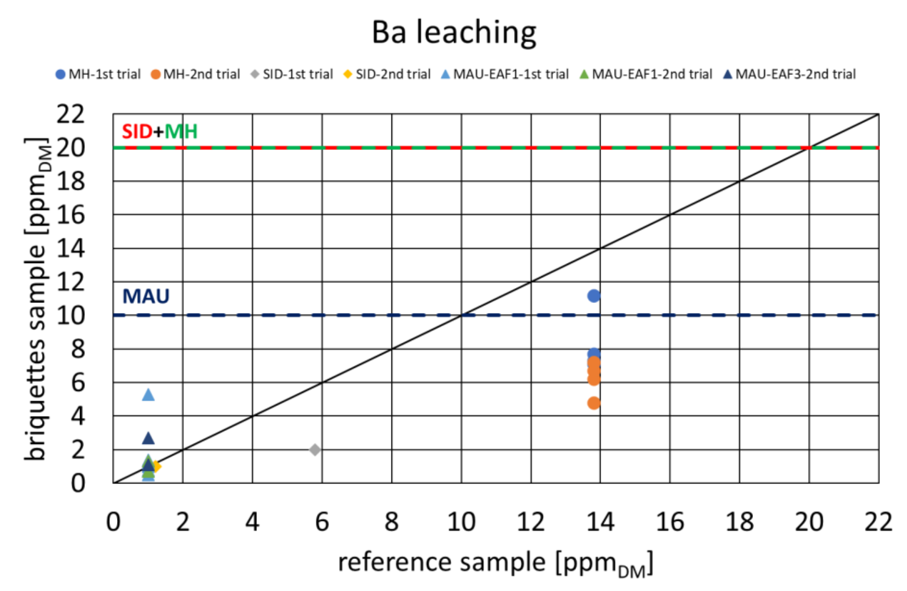
Parameter	Electric conductivity	pH-value	Cr tot	F-	V	Mo	Ba	W
Unit	µS/cm		µg/l	µg/l	µg/l	µg/l	µg/l	µg/l
Limits*	1500	10-12.5	100	2000	250	250	1000	-
1st trial								
MAU R-1	329	11.22	<50	970	70	<50	100	90
MAU R-2	226	11.04	<50	1150	<50	<50	110	120
MAU 1000 500-3	430	11.33	<50	1590	<50	<50	120	100
MAU 1000 500-4	238	11.02	<50	950	80	<50	140	90
MAU 800 500-1	254	11.05	<50	1070	60	<50	70	90
MAU 800-500-2	500	11.38	<50	1220	<50	<50	100	60
MAU 500 500-1	302	11.23	<50	1090	<50	<50	80	110
MAU 500 500-3	301	11.17	<50	1150	<50	<50	70	50
MAU 0 2000-1	76	10.43	<50	930	<50	<50	<50	50
MAU 0 2000-2	560	11.53	<50	1410	<50	<50	130	70
MAU 0 2000-3	205	10.92	<50	980	50	<50	530	100
2nd trial								
MAU E1 R-1	203	11.04	<50	1320	<50	<50	240	100
MAU E1 R-2	430	11.36	<50	1280	80	50	100	120
MAU-E1 0 2000-1	191	10.94	<50	1170	<50	<50	130	100
MAU-E1 0 2000-4	180.2	10.93	<50	1160	<50	<50	70	50
MAU E3 R-1	449	11.4	<50	1330	80	110	100	80
MAU E3 R-2	331	11.19	<50	1120	70	60	130	200
MAU E3 0 2000-1	431	11.29	<50	1100	<50	<50	110	200
MAU E3 2000-4	320	11.18	<50	1120	50	110	270	260

* Verwertung von Elektroofenschlacke (EOS), Umweltfachliche Kriterien - Z 2 Eingeschränkter Einbau mit definierten technischen Sicherungsmaßnahmen

RESULTS – LEACHING TEST



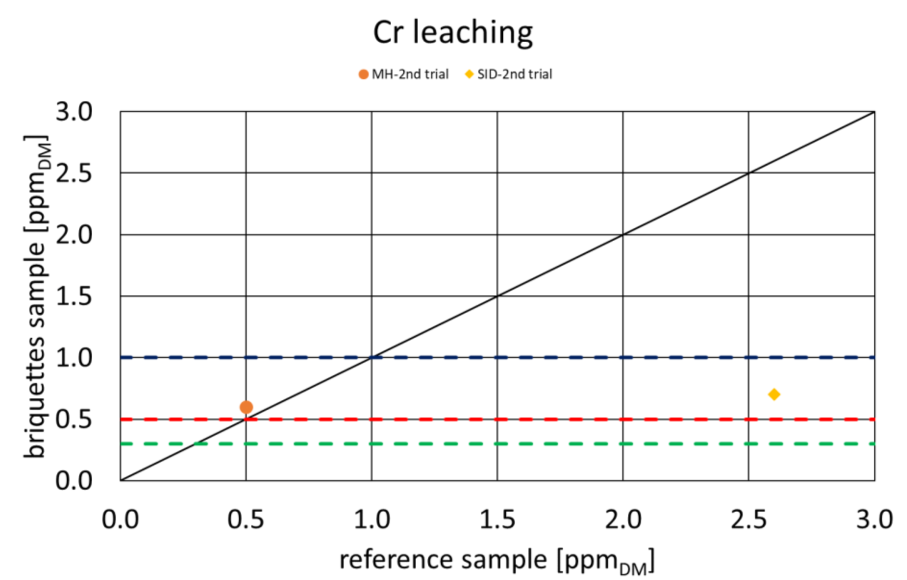
RESULTS – LEACHING TEST



- analisys concentrated on six elements which shown relevant concentration during the leaching
- Ba, Cr, F, Mo, V and W
- samples below detection limit were excluded
- only stricter leaching limits were plot

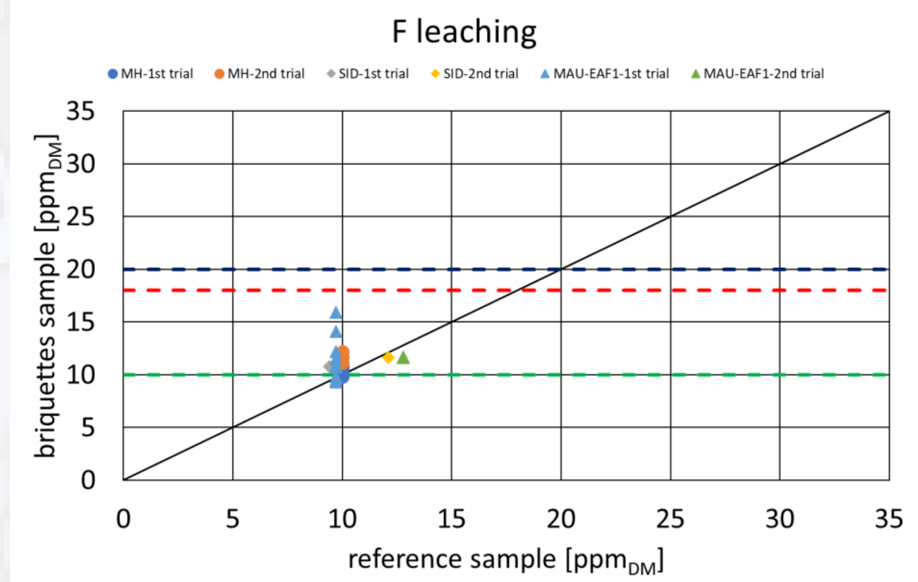
- Ba:
  - slag samples with briquettes behave generally better than reference
  - no samples over the limits

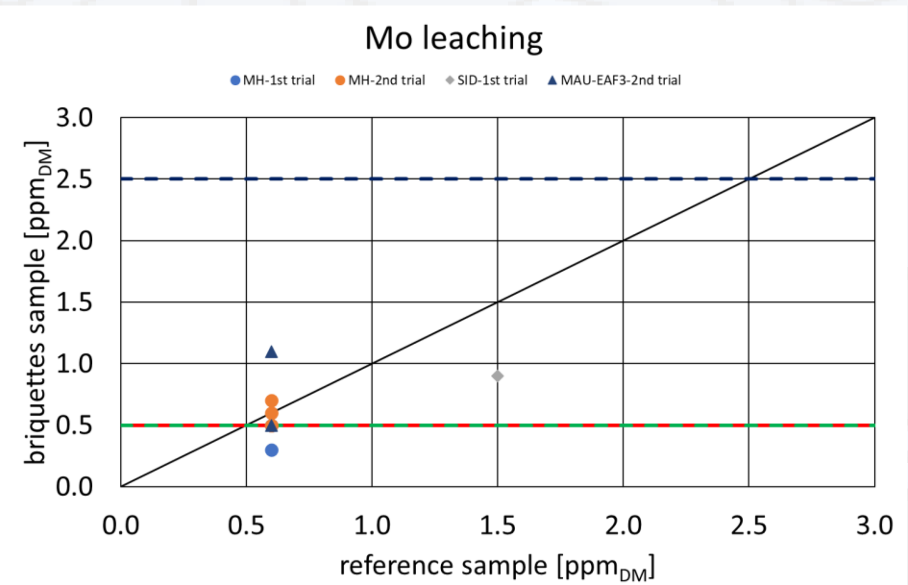
- Cr:
  - only two samples over their respective limits
  - behavior similar or better than reference



RESULTS – LEACHING TEST

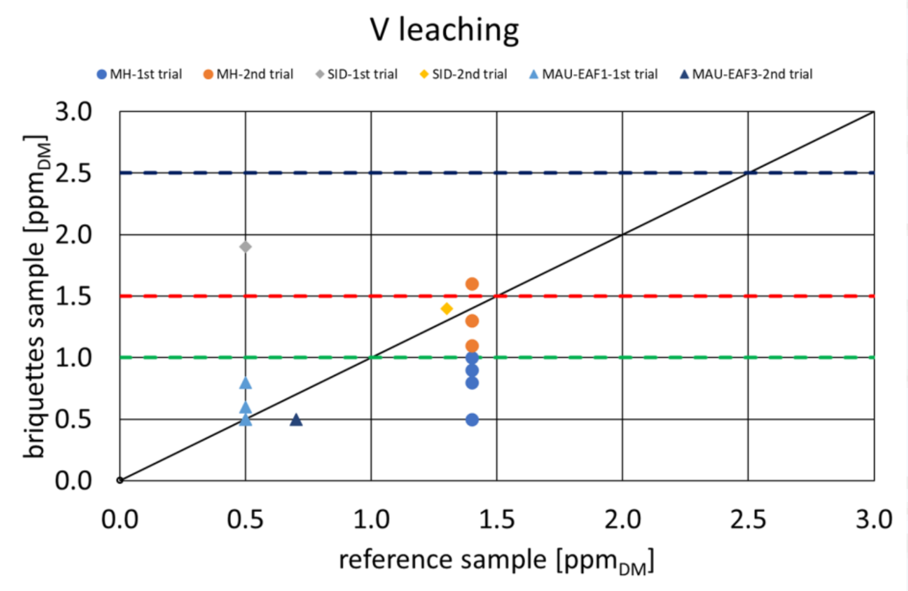
- F:
  - unique parameter got worse after briquettes charge
  - exceeding limits only for MH samples





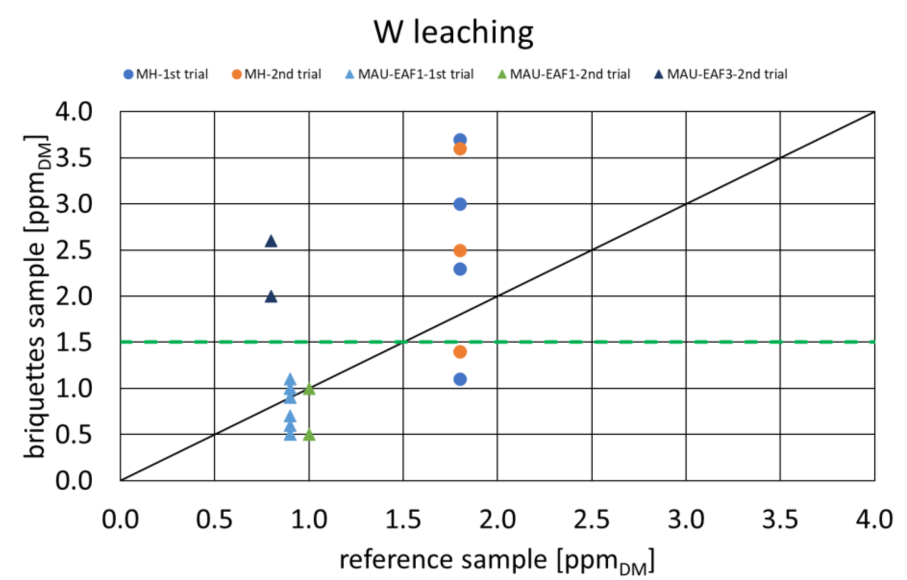
- Mo:
  - not a clear effect of briquettes on its leaching charge
  - only few samples exceeded the limits

RESULTS – LEACHING TEST



- V:
  - Like Ba, slag samples with briquettes behave generally better than reference
  - Some samples exceeding the limits

- W:
  - not a clear influence of briquettes charge on this elements
  - high data scattering



CONCLUSIONS

- slag samples with briquettes exhibit generally the same chemical, crystallographic and morphological properties than reference samples
- the addition of briquettes dos not seem to cause any considerable variation
- detected variability is due to heterogeneity of the slag itself that's depend on the scraps heterogeneity
- Slag leaching behavior it is not affected by briquettes addition

influence of raw-material fines recirculation into the EAF on slag quality is

NEGLIGIBLE