A Computational study to estimate the possibilities to improve utilisation of stainless steelmaking slags

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Abstract: Utilisation of solidified AOD slags from stainless steelmaking is hindered by dicalcium silicate, which causes disintegration and dusting of solidified slag. Utilisation of AOD slags may be improved by changing the slag composition to the composition range in which dicalcium silicate is not formed. Instead of changing the composition during the AOD process - which is not favourable for the process optimization - it is possible to mix AOD slag with other slags in order to obtain compositions more suitable for slag utilisation and hence improve the material efficiency of stainless steelmaking. Integration of ferrochrome and stainless steel production in the Outokumpu Tornio plant enables the mixing of AOD slags with submerged arc furnace (SAF) slags before the slags are solidified. In addition to changing the slag composition to the composition range that favours its utilisation, the combination of two slags enables the reduction of chromium from both slags with a single treatment. Without the recovery of chromium, the chromium losses would be significant especially with the SAF slags. The purpose of this study was to study the behaviour of the slag systems in which AOD and SAF slags are mixed with different ratios. Firstly, the phase compositions of different slag compositions in different temperatures were evaluated. Secondly, reduction of chromium from different slag systems using coke, methane and ferrosilicon as reductants was evaluated in a constant temperature. According to the results the formation of dicalcium silicate is avoided if the amount of SAF slag is more than 30 %. However, the liquidus temperature of the slag mixture increases with increasing SAF slag -content, which defines an upper limit for the amount of SAF slag. Chromium can be reduced from the slag mixtures with all the considered reductants, although the amounts of reductants required for reduction varied greatly.

1. INTRODUCTION
1.1. Studied materials
Outokumpu Stainless produces annually approximately 1.2 – 1.3 million tons of stainless steel in its integrated steel plant in Tornio, Finland. The plant consists of ferrochrome plant (sintering plant and submerged arc furnaces, SAF) and stainless steel plant (electric arc furnaces, EAF; chromium converter, CRC; AOD-converters; ladle treatments; continuous casting, CC; hot and cold rolling).

Materials studied in this research were slags from the SAF and AOD processes, both of which are formed approximately 0.2 million tons annually. Average chemical compositions of the AOD and SAF slags from Outokumpu Tornio stainless steel plant are presented in Table 1 together with the compositions of mixed slags with different portions of AOD and SAF slags.

Table 1. Average chemical compositions of AOD and SAF slags as well as chemical compositions of slag mixes.

Portion of slag [%]		Chemical composition [wt-%]							
SAF	AOD	CaO	SiO$_2$	MgO	Fe$_2$O$_3$	Cr$_2$O$_3$	Al$_2$O$_3$	TiO$_2$	CaF$_2$
0	**100**	**53.6**	**26.6**	**7.7**	**1.0**	**1.0**	**1.9**	**0.5**	**7.7**
20	80	43.3	27.3	10.8	1.9	3.4	6.8	0.4	6.2
30	70	38.1	27.6	12.3	2.4	4.6	9.2	0.3	5.4
40	60	33.0	28.0	13.8	2.9	5.8	11.6	0.3	4.6
50	50	27.8	28.3	15.4	3.3	7.1	14.0	0.2	3.9
60	40	22.7	28.7	16.9	3.8	8.3	16.4	0.2	3.1
70	30	17.5	29.0	18.4	4.3	9.5	18.8	0.1	2.3
80	20	12.3	29.3	20.0	4.8	10.7	21.2	0.1	1.5
100	**0**	**2.0**	**30.1**	**23.0**	**5.7**	**13.2**	**26.0**	**0.0**	**0.0**

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1.2. Aim of the study

The aim of this study was to estimate how the utilisation of the SAF and AOD slags could be improved with mixing of the slags. The goal is to avoid the formation of dicalciumsilicate during the solidification, since it causes disintegration [1, p. 250] and dusting of solidified slag thus hindering its utilisation. Additionally, by mixing the slags before solidification it would be possible to reduce oxidized chromium from both slags with a single treatment.

Estimations were based on thermodynamic computations executed with FactSage version 7.1 and its FactPS and Ftoxid databases. Compositions presented in Table 1 were used as initial compositions.

2. MIXING OF SLAGS

First, thermodynamically stable phase compositions as a function of temperature were computed for the slag systems with the compositions presented in Table 1. As a result, the portion of molten phase in different temperatures as a function of AOD/SAF –slag-ratio was obtained, *cf.* Fig. 1. Solid phases stable in each temperature were also determined, although they are not presented in Fig. 1. If the slag treatment is assumed to take place at approximately 1600°C, the portion of molten phase is decreased from over 95% to approximately 75%, when the AOD/SAF –slag ratio is changed from 80/20 to 20/80. The only solid phase stable in this temperature – and higher temperatures – is a spinel phase containing Mg, Fe, Al and Cr. According to the results, dicalcium silicate is not formed until in lower temperatures and it does not exist at all in the slag mixes with more than 30% of SAF slag.
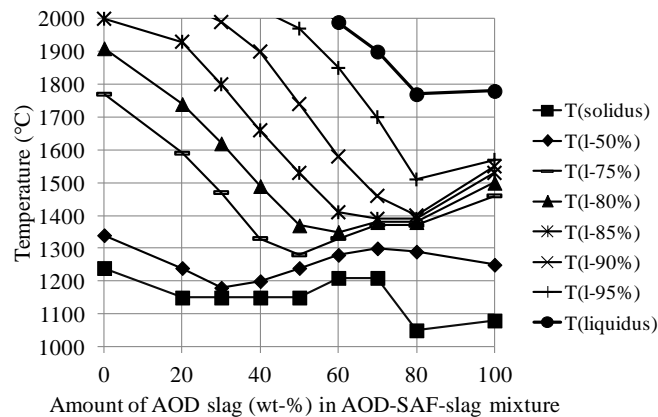

Figure 1. The portion of molten phase in different temperatures as a function of AOD/SAF –slag ratio.

3. REDUCTION OF CHROMIUM FROM MIXED SLAGS

Secondly, reduction of oxidized chromium from the slag mixes was studied with four different reductants: carbon, methane and ferrosilicon with two silicon contents. 100g of slag mixes with AOD/SAF –slag ratios from 20/80 to 80/20 was defined as a basis for all the computations. Amounts and compositions of stable phases at 1600°C were calculated as a function of the amount of reductant. An example of the results is shown in Fig. 2, in which distribution of chromium in different phases (*i.e.* molten oxide/slag, molten metal and solid spinel) using different reductants is shown for the slag mixture with AOD/SAF –slag ratio 50/50. According to the results, almost all the chromium is initially in the spinel phase, although its amount is small compared to the amount of molten oxide phase. As the amount of reductant is increased, the amount of chromium in the spinel phase decreases whereas its amount in the molten oxide phase increases accordingly. As the amount of reductant is further increased, chromium oxides are reduced and chromium ends up in the molten metal phase.

The amounts of different reductants required in the reduction of chromium can be compared using Fig. 3. In this figure the reduction has been assumed to begin with a reductant addition with which at least 1% of the chromium has been reduced into the metal phase and the reduction has been assumed to be complete with the reductant addition with which at least 99% of the chromium is in the metal phase. It is seen from Fig. 3 that amounts of different reductants required to reduce chromium from different slag mixtures vary considerably. First of all, since the amount of chromium is much higher in the SAF slag in comparison to AOD slag (*cf.* Table 1), less reductants are required for the slag mixtures with higher AOD/SAF –slag ratios. Secondly, the amount of carbon required for the

reduction of chromium is smaller than the amount of methane, whereas the amounts of two kinds of ferrosilicon are even higher. It is also seen from Fig. 3 that with the excess use of reductants the formation of solid carbon (soot) is possible when using carbon or methane as a reductant.
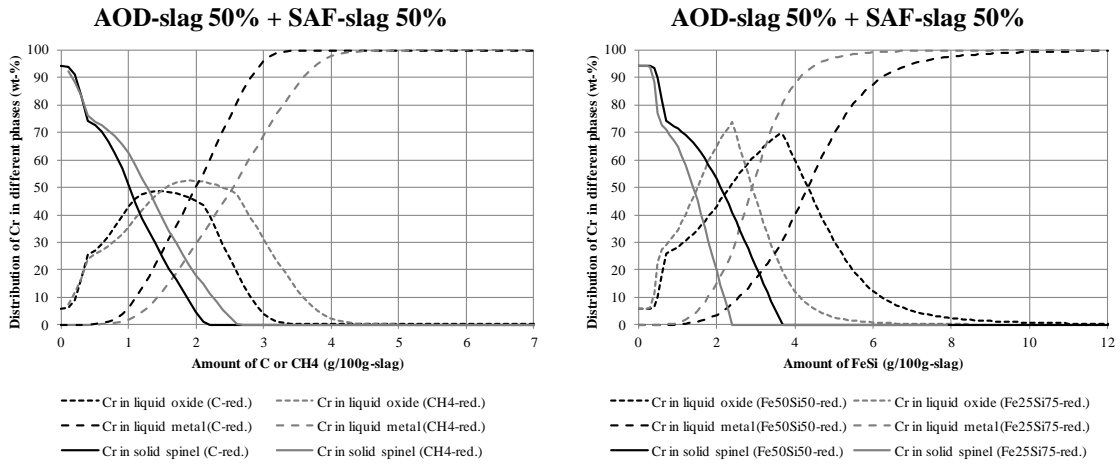

Figure 2. Distribution of Cr in different phases (*i.e.* molten oxide/slag, molten metal and solid spinel) using C, CH$_4$ and two types of FeSi as reductants. Slag mixture with AOD/SAF –ratios of 50/50 is shown as an example.
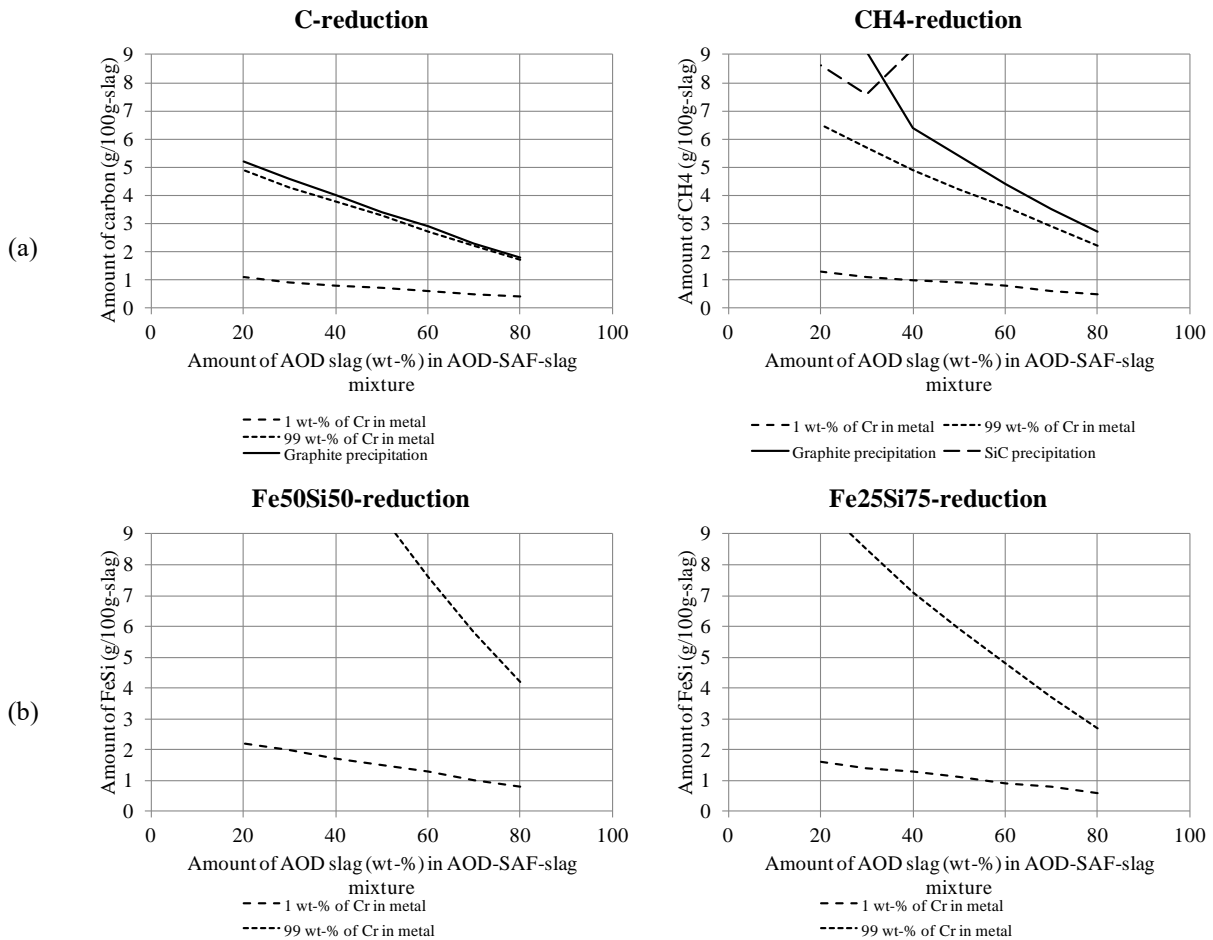

Figure 3. Amounts of different reductants required to reduce chromium from the slag mixtures with varying AOD/SAF –ratios: (a) C or CH$_4$ as reductant, (b) FeSi as reductant.

Finally, the amount and composition of the metal phase were estimated while using different AOD/SAF –slag ratios and reductants. An example of these estimations is shown in Fig. 4, in which the slag mixture with AOD/SAF –slag ratio of 50/50 is chosen as an example. It is seen from Fig. 4 that as the amounts of reductants are increased, both amount and chromium content of the metal phase are increased until nearly all chromium is reduced. With carbon and methane reduction the amount of

metal phase does not increase with excess addition of the reductant, whereas the excess addition of ferrosilicon leads to increased amount of metal with lower chromium contents due to diluting effect of iron and silicon. A small decrease in the chromium content with small excess additions of carbon and methane is due to reduction of SiO_2 from the slag phase.
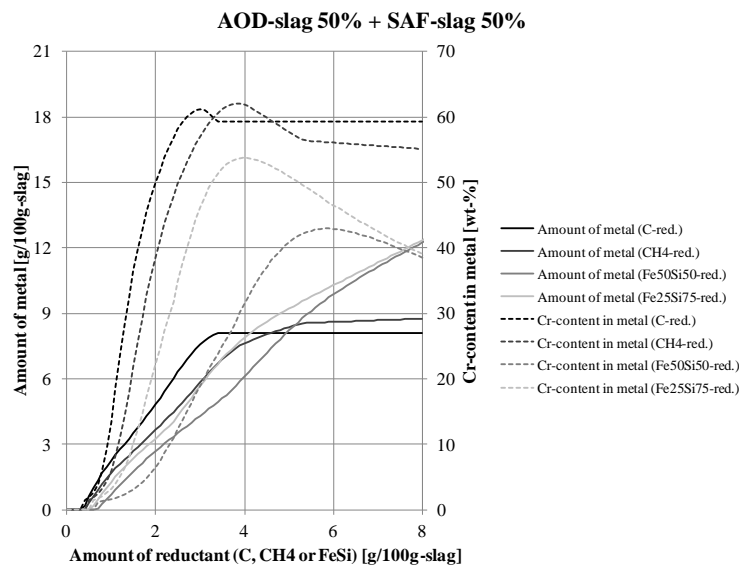

Figure 4. Amounts and chromium contents of the molten metal phase as a function of amount of reductant used to reduce the slag mixtures. Slag mixture with AOD/SAF –ratio of 50/50 is shown as an example.

4. SUMMARY

The main conclusions made based on the results of the computations are collected in Table 2. This study was based on thermodynamic computations and does not consider if reduction rates are different depending on whether chromium is in molten slag or in solid spinels. Furthermore, it is not yet analysed if chromium containing metal droplets exist in the slag materials. According to rough heat balance estimations, reduction with carbon and methane would require extra heating – especially with low AOD/SAF –slag ratios – whereas some heat is released in the reduction with ferrosilicon.

Table 2. Conclusions of this study.

| | AOD/SAF –slag ratio | | | Reductant | | | |
	Low	50/50	High	C	CH$_4$	Fe50Si50	Fe25Si75
Pros	No risk for 2CaO·SiO$_2$.	Equals with the formed amounts. No risk for 2CaO·SiO$_2$.	Less reductants required. Lower liquidus temperature	Smallest amount required for reduction. High Cr-content in metal.	Small amount required for reduction. High Cr-content in metal.	No risk for C- or SiC-precipit.	No risk for C- or SiC-precipit.
Cons	More reductants required. Higher liquidus temperature		Risk for 2CaO·SiO$_2$.	Risk for C-precipit.	Risk for C- and SiC-precipit.	Highest amount required for reduction. Low Cr-content in metal.	High amount required for reduction. Low Cr-content in metal.

REFERENCES
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