Phase relationship of quaternary system FeO-Al_2O_3-SiO_2-“V_2O_3“ at 1873 K and its impact during melting of H-DRI for possible vanadium extraction.

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EXTENDED ABSTRACT

The European Union has listed vanadium (V) as one of the critical raw materials for the transition to a future green society, as stated in the Critical Raw Material Act, written by Grohol and Veeh. In the steelmaking industry based on V-containing iron ore, V is a possible by-product from the slag. A requirement for slags to be suitable for V extraction is a V content preferably above 8 wt% as V_2O_3 and a phosphorus (P) content below 0.1 wt% as P_2O_5. Hence, it is important to keep V in the slag phase while the P is moved to the metal phase during the steelmaking process.

The present research group has carried out parallel works to increase the understanding on how to concentrate V in the slag during steelmaking, while reaching a low P content. The works have been a part of the HYBRIT research program, a joint venture between the iron ore producer LKAB, steel producer SSAB and electricity producer Vattenfall, with the aim to pioneer fossil-free steel production. The starting point of the raw material has therefore been the existing high quality LKAB iron ore pellet named KPRS, designed for direct reduction (DR) shaft furnace technology. The composition of KPRS pellets can be seen in Table 1.

TABLE 1 – Composition of KPRS, as written in the 2021 LKAB Product Catalogue.

	Fe	**SiO_2**	**CaO**	**MgO**	**Residual oxides**
wt%	67.8	0.80	0.90	0.65	1.01

KPRS was first reduced in pure hydrogen at 900 °C to different reduction degrees in a vertical resistance-heated furnace. The hydrogen reduced iron pellets (H-DRI) were then melted, one by one, in a high temperature resistance-heated furnace at temperatures between 1500-1600 °C, and quenched after different times, to study the melting progression. It was found that the unreduced oxidic components (CaO, SiO_2, MgO, remaining FeO etc.) inside the H-DRI formed an autogenous slag inside the pellet already prior to the melting of the iron grains. The autogenous slag was found to flow in the porous network inside the H-DRI, between the reduced iron grains. Upon the melting of iron, numerous of autogenous slag droplets were found distributed in the liquid metal, generating a huge surface area between slag and metal.

The experimental results also showed that the autogenous slag system based on the present H-DRI contained in general terms FeO-CaO-SiO_2-MgO. The CaO/SiO_2 ratio was approximately 1.2, FeO content varying between approximately 20 and 70 wt% depending on reduction degree, and MgO saturated at approximately 10 wt%.

H-DRI was also melted batchwise to study the resulting V and P partitions based on oxygen potential fixed by the FeO/Fe equilibrium in the slag using a closed crucible. It was unfortunately found that it is difficult to sufficiently separate V and P using the KPRS as raw material, independent of the oxygen potential. Too much P was still found in the slag.

In the subsequent work, the separation of V and P was studied in a novel slag system based on FeO-Al_2O_3-SiO_2-V_2O_3, i.e., CaO is replaced by Al_2O_3. Examples of weigh-in slag compositions can be seen in Table 2.

TABLE 2 – Examples of weigh-in slag composition.

	FeO_x wt%	**SiO_2 wt%**	**Al_2O_3 wt%**	**V_2O_3 wt%**	**$[P]_{Fe}$ wt%**
Slag 1	40	31.25	18.75	9.99	0.20
Slag 8	10.74	43.35	26.05	19.85	0.89
Slag 14	11.05	24.70	54.42	9.84	0.82

In the experiments, 10 grams of slags were allowed to react with 30 grams of iron containing P additions, as shown in Table 2, at a temperature of 1873 K inside a high temperature resistance-heated furnace. The oxygen potential was fixed by the system through the FeO/Fe equilibrium by closing the crucible with a lid. The pO_2 was calculated using Thermo-Calc, based on XRF analysis. Almost all P was found in the metal phase, while a V_2O_3 content higher than 8 wt% was obtained in the slag, as shown by Table 3. I.e., the system was found promising for the separation of V and P.

TABLE 3 – Examples of slag and iron analysis after equilibration.

	XRF analysis					**OES analysis**		**pO_2 x 10^{11} atm**
	FeO wt%	**SiO_2 wt%**	**Al_2O_3 wt%**	**V_2O_3 wt%**	**P_2O_5 wt%**	**$[P]_{Fe}$ wt%**	**$[V]_{Fe}$ wt%**	
Slag 1	30.1	27.3	38.2	4.4	<0.01	0.159	0.069	9.41
Slag 8	21.9	31.3	37.9	8.8	<0.01	0.300	0.329	4.82
Slag 14	16.9	27.1	49.3	6.7	<0.01	0.300	0.153	4.12

The results also showed that V could be found in different phases in the slag. Unfortunately, the available literature of phase diagrams for vanadium containing slags are limited. Since the phase relationship is likely to impact the aftercoming V extraction, it is necessary to study which phases are stable at relevant oxygen partial pressures, and how much V each phase contain. Therefore, the pseudo ternary phase diagrams Al_2O_3-SiO_2-“V_2O_3”, FeO-SiO_2-“V_2O_3” and Al_2O_3-FeO-“V_2O_3” were studied in another subsequent work. The fourth system Al_2O_3-FeO-SiO_2 was found sufficiently studied in the literature, compiled in the Slag Atlas. The construction of phase diagrams was based on experiments conducted at 1873 K and the different oxygen partial pressures 3.4×10^{-11}, 3.3×10^{-10} and 3.4×10^{-9} atm, controlled by a CO/CO_2 mixture. After equilibration, the samples were quenched in oil. The phase compositions, analysed by wavelength-dispersive spectroscopy (WDS), were used to construct relevant phase diagrams based on each slag system and oxygen partial pressure. Since V is multi-valent, its valence state at equilibrium can vary depending on oxygen partial pressure, temperature, and slag composition. In the present work, "V_2O_3" is used for giving the content of vanadium. The valence state has although not been analysed, thus the use of citation marks around “V_2O_3” to illustrate the uncertainty.

In the pseudo ternary phase diagrams based on the quaternary system Al_2O_3-FeO-SiO_2-“V_2O_3”; mullite, spinel Al_2O_3-corundum, V_2O_3-corundum, cristobalite, and liquid were found. Among these phases, only cristobalite had zero trace of V, and only small amounts were found in the liquid.

In this work, the Al_2O_3-SiO_2-“V_2O_3” system is presented as example. The oxygen potential had no profound effect on the Al_2O_3-corundum+V_2O_3-corundum+mullite and the V_2O_3-corundum+cristobalite+liquid equilibria. On the other hand, the equilibrium between V_2O_3-corundum, mullite and liquid was affected. A decreased oxygen potential resulted in higher contents of Al_2O_3 and slightly higher contents of V_2O_3 in the liquid phase, as well as slightly higher contents of Al_2O_3 in V_2O_3-corundum and mullite. Since V is multi valent, the oxygen partial pressure will decide the fraction of the different valance states of V in the slag. The different valence states of V can be dissolved into different phases, resulting in a change in the phase diagram as a result of changed oxygen partial pressure.

For vanadium extraction, V_2O_3 must first be roasted (oxidized) to V_2O_5 for the leaching process to work. It is therefore important to understand which phases that are easier, or even possible, to roast. The research must henceforth be carried out systematically. The phase diagrams constructed in the present work will be used to suggest slag compositions which result in high V content. The resulting slags will then be studied in a roasting process. The roasting process will in turn give feedback regarding if the resulting V-containing phases were easy to roast or not, which will result in new suggestions of slag compositions based on the phase diagram. The slag compositions that resulted in highest V content had V found in the solid phases spinel, mullite and corundum. These phases are therefore the most interesting in the initial stage of the future studies on roasting.

At the same time as V needs to be concentrated in the slag, P needs to be moved to the steel. The first study regarding melting mechanisms of H-DRI showed that an autogenous slag is formed and flows inside the H-DRI prior to the melting of iron. As iron melts, slag is distributed as droplets in the iron melt, generating a huge reaction surface area between the slag and metal. The kinetic conditions for moving P from the slag to metal is therefore potentially excellent and the separation of V and P is thus promising.

Since V is mainly found in solid phases, a slag suitable for V extraction will assumably result in a slag with high fraction of solids, resulting in high viscosity. In an industrial point of view, a highly viscous slag can be problematic to handle in the production and can be associated with high costs to ensure safe production. An optimized slag practice for maximum V extraction is therefore important to reach maximize profitability.

In addition, the proposed production route will result in an iron melt containing high content of P. A two-slag-practice is therefore necessary to produce a clean steel with low P and meet the demands of the steel producer. The first slag, based on the autogenous slag, will in this scenario extract V to the slag while P is moved to the steel melt. This slag would then be removed from the furnace, after which a second slag will be added. The second slag will be closer to a traditional slag for phosphorus removal, with high oxygen potential and a basicity of more than 2.

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