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Feasibility of recovering metals from associated slags

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After smelting, the associated mineral ore accompanying Valuable Metal Compounds (VMC), such as titania and borate in BF., most of the VMC were separated from the metal into the molten slag that is an associated slags. Based on several case studies in laboratories and in a practice in a pilot plant on the associated slags , there occur a feasibility to recovery VMC from the slags by a new process- Selective Precipitation Technique (SPT) on which three continuous steps are involved: (1) The selective enriching the dispersed VMC into a designed mineral phase in the molten slag; (2) The selective coarsening the designed mineral phase with large crystal grain size; (3) The selective separating the coarsen phase from tailing by mineral dressing or hydrometallurgical process . Some results on the recovering the VMC from the associated slags by SPT were summarized as examples in present paper.
Keywords: selective precipitation technique, associated slag, recovering metals from slag.

Introduction

The associated mineral ore accompanying Valuable Metal Compounds (VMC) have been usually treated in a smelting furnace ,such as Blast Furnace, Reverberatory, Blowing Furnace, hence the VMC were mostly concentrated into the molten associated slags and separated from liquid metals. So the associated slags become an important man-made resources (Table I), in which the VMC exist dispersively in various mineral phases with fine grain size[1–4].

Due to complex mineralogy and very fine mineral dissemination of the associated slags, it is difficult to recovery the VMC from the slags by metallurgical or mineral process conventionally .

Based on several case studies in laboratory and practices in pilot plant on the associated slags , there occur a feasibility to recovery the VMC from the slags by a new process-Selective Precipitation Technique (SPT) on which three continuous steps are involved (in Figure 1).

- The selective enriching the dispersed VMC into a designed mineral phase in the molten slag
- The selective coarsening the designed mineral phase with large crystal grain size
- The selective separating the coarsen phase from tailing by mineral dressing or hydrometallurgical process.

In present paper some results on the recovering the VMC from the slags by SPT were summarized as examples respectively .

Table I
Chemical composition of the associated slags (wt%)

Slag	CaO	SiO_2	Al_2O_3	MgO	B_2O_3	TiO_2
Ti-slag	27–28	22–25	14–15	7–8	0	22–23
B-slag	5–10	5–35	5–10	35–45	12–15	0

Recovery titania from Ti-slag[6–8]

China is rich in titanium mineral resources, but 95% of that were deposited in the form of associated mineral 'Vanadium-Titanium Magnetite Ore' and located at west-south part of country named 'Panzhihua city'. At present the ore was smelted in Blast-Furnace at Panzhihua Iron &

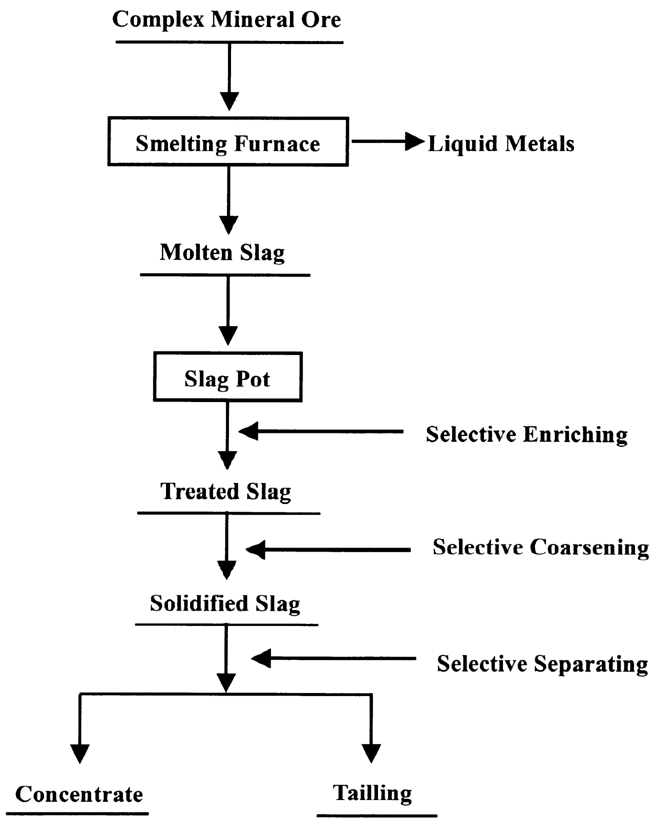


Figure 1. Flow chart for treatment of associated slags by SPT

steel Company, as result, the titania (TiO_2) in the ore was mostly concentrated into molten slag and separated from molten pig iron. The associated BF slags containing 22–23% TiO_2 are a potential feedstock for extracting titania.

However, the quality of the associated slags was so poor (in Table I) that the slags as a feedstock were suitable neither for producing a titania pigment nor for making a slag cement. The slags have been accumulated over 50 million tons just now and amount of the slags is still increasing at a rate of 3 million tons a year, that results in a great waste of titanium-resources and environment pollution seriously[1–2].

The reason of the slags not being utilized is slag's characteristics which are as followed: the dispersed distribution of titania in various mineral phases (in Table II); very fine grains size (smaller than 10 µm)of the mineral phases and complex interfacial combination.

It was identified by EPMA and XRD that several mineral phases were existed in the associated slags and the titania was dispersed in various mineral phases as shown in Table II[12].

Selective enriching[15]

It is clearly from Table II that the Perovskite phase containing the largest amount of titania is reasonably to be chosen as the designed phase into which the titania dispersed in various mineral phases will be enriched.

After adjusting the slag's composition (basicity R = CaO/SiO_2) and injecting oxygen gas to molten slag, the most of titania in the slags were enriched into the Perovskite phase and the morphology of the Perovskite was obviously varied (in Figure 3). As result, the distribution of titania in the Perovskite phase was increased from original 48.0 % to final 100 % (in Figure 2 and Table III).

Selective coarsening[6,10,12]

The coarsening the Perovskite phase in molten slag can be achieved by optimizing condition such as start-blowing temperature and oxygen injection time, as shown in Figures. 4 and 5 respectively.

It was determined by Imagine Analysis that the average grain size of the Perovskite phase was changed from original 2~10 µm to final 60~80 µm after the optimizing treatment.

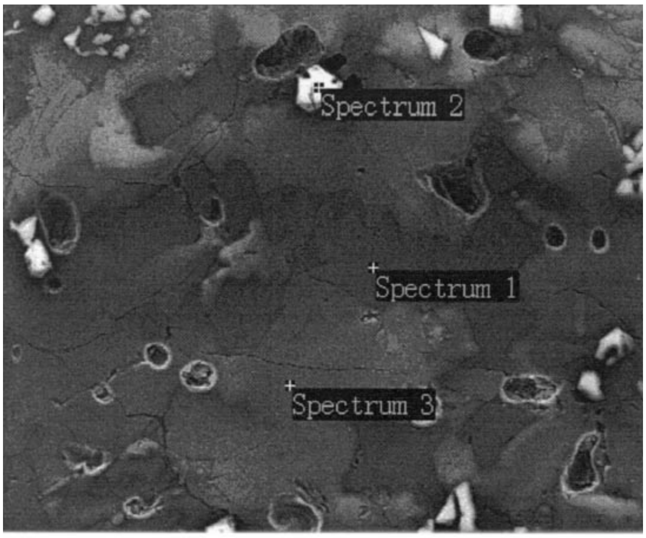
Selective separating[9]

Based on the study of the mineralogy of the Perovskite and the interfacial combination with other mineral phases in the slags, the products (concentrates and tailings) were obtained by dressing process (in Table IV).

The concentrates have already been used as a feedstock for producing the titania-enriched material[17,16] (in Table V) which could be used as raw material for making the titanium dioxide pigment by chloride route, and the tailings as a filler for making the slag cement.

Recovering boron form b-slag

64% of boron mineral resources is in the form of Ludwigite ore and deposited around the northeastern part of China. When the ore was carefully treated in a pilot blast furnace , all of the magnesia and 90 % of the boron in the ore were concentrated in the molten slag and separated from liquid pig-iron .Hence the urgent need is to extract boron from the associated slags efficiently.



Electron Image 1

Figure 2. Microstructure of the treated sample

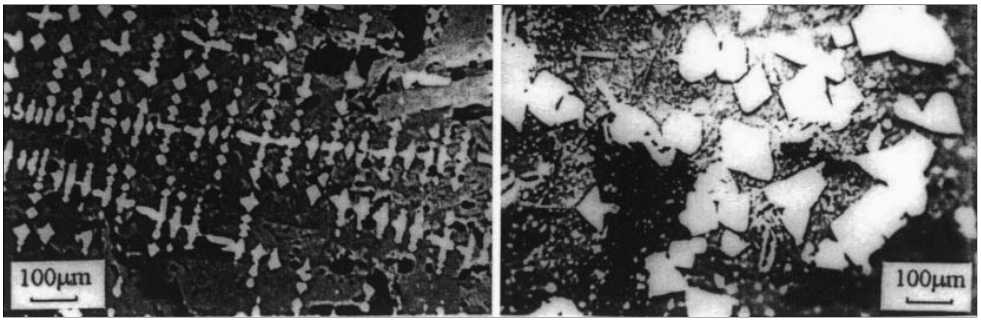
Table III
All elements analysed by EPMA

Spectrum	O	Mg	Al	Si	Ca	Ti	Total
Spectrum 1 (Perovskite)	36.26				28.86	34.89	100.00
Spectrum 2 (Spinel)	51.73	12.96	35.31				100.00
Spectrum 3 (Wollastonite)	53.14	7.50	10.97	15.06	13.33		100.00

All results in weight per cent

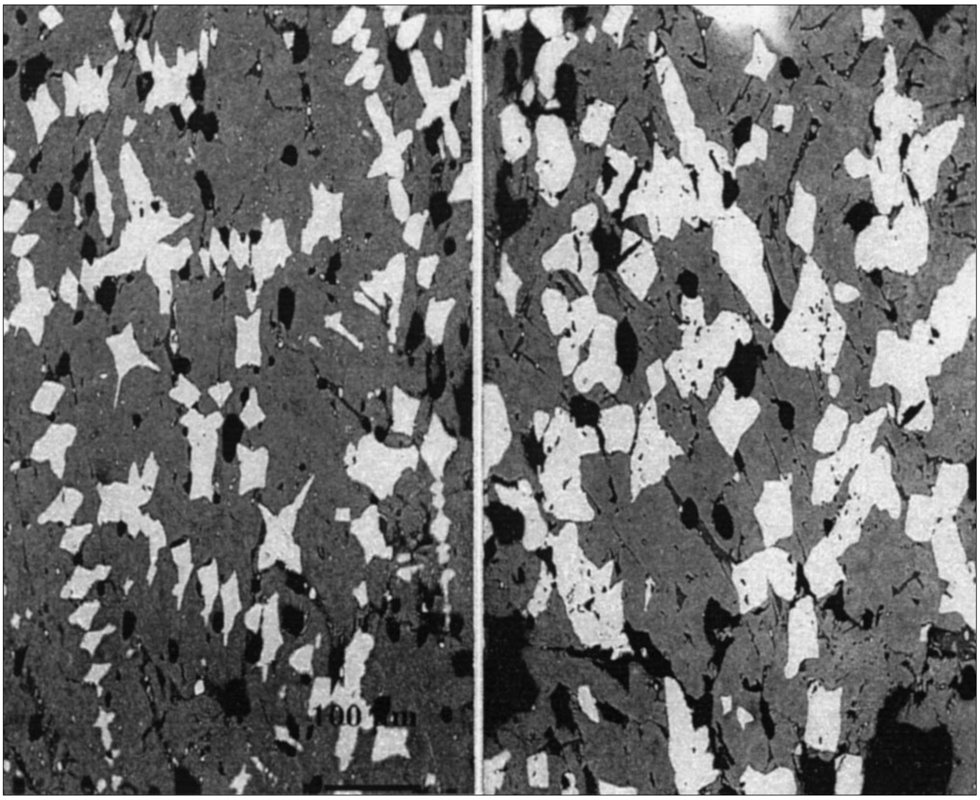
Table II
The titania dispersed in various mineral phases (wt%)

Name of mineral phases (formula)	Content of the titania	Distribution of the titania	Dispersion of the titania in the slags
Perovskite $(Ca_{0.93}\ Mg_{0.04}\ Al_{0.03}\ Fe_{0.01})_{1.01}\ (Ti_{0.94}\ Al_{0.04}\ Si_{0.02})_{1.00}\ O_3$	55.8	48.0	11.6
Titanaugite $(Ca_{0.96}\ Mg_{0.53}\ Ti_{0.46}\ Fe_{0.04}\ M_{0.01})_{2.00}\ [(Si_{1.28}\ Al_{0.72})_{2.00}O_6$	15.5	37.9	9.1
Ti-rich Diopside $(Ca_{0.35}\ Mg_{0.66}\ Ti_{0.45}\ Fe_{0.03}\ Mn_{0.01})_{2.00}\ [(Si_{0.93}A_{l0.84}\ Ti_{0.23})_{2.00}O_6]$	23.6	5.7	1.4
Spinel $(Mg_{1.007}\ Fe_{0.018}\ Ca_{0.010}\ Mn_{0.005})_{1.040}\ (Al_{1.741}\ Ti_{0.131}\ Si_{0.032}\ V_{0.008}\ Cr_{0.001})_{0.913}\ O_4$	7.2	1.1	0.3
Titanium Carbide Ti(C, N)	95.7	4	1.0
Sum		100	23.4



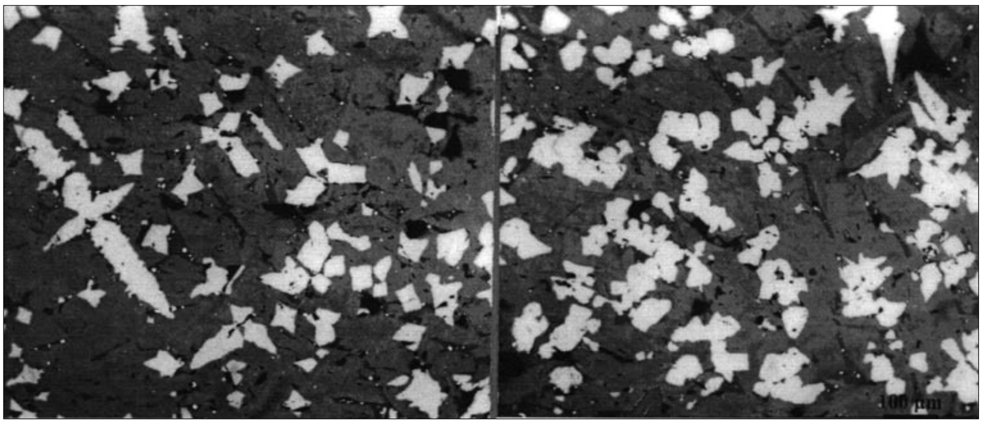
(a) (b)

Figure 3. The morphology of the perovskite phase as (a) R = 1.0 and (b) R = 1.4



(a) 1400°C (b) 1430°C

Figure 4. Micrographs of the treated samples with various start blowing temperature



(a) 2 min (b) 6 min

Figure 5. Micrographs of the treated samples with various oxygen injection times

Table IV
Chemical composition of the concentrates and the tailings (wt%)

Product	TiO_2	CaO	MgO	FeOx	$Al_2O_3 + SiO_2$
Concentrates	35–45	30–35	8–9	3-5	18–6
Tailings	8–11	15–25	8–10	7–10	60–4-

Table V
Chemical composition of the titania-enriched material (wt%)

	TiO_2	CaO	MgO	Al_2O_3	SiO_2	Fe_2O_3
Titania-enriched material	92–95	0.05	0.05	2.65	0.82	1.17

It was found by experiments that the efficiency of extraction of boron (EEB) from slag was directly related to both the operation conditions like slag's composition and heat-treatment temperature as well as the precipitating characteristics of the boron compounds, such as amorphous or crystalline phases.

The EEB is low when the molten slags were quickly cooled and then the most of the boron compounds are existed in the form of amorphous phases, while the EEB is high when the slags were slowly cooled and then the boron compounds are in the form of crystalline phase-Suanite ($2MgO{\cdot}B_2O_3$), which is reasonably chosen to be the designed phase.

Chemical composition[2,13]

It can be seen in Figure 6 that the composition of slags having high EEB are just located along the line between $2MgO{\cdot}SiO_2$ and $2MgO{\cdot}B_2O_3$.

The farther the composition deviates from the line, the lower the EEB is.

Temperature of heat treatment[4,5]

During cooling process a precipitation of Suanite crystalline is dependent on the nucleation rate I and crystal growth rate U.

When the temperature was in the range of 1100–1240, according to the kinetic calculation[4,11], both I and U can approach to higher values simultaneously. Therefor, for Suanite crystalline precipitation, 1100°C is the optimum temperature for heat treatment. The calculated optimum temperature is in good agreement with the experimental results (Figure 7).

Additive[13–14]

The microstructure of the sample without any additive was shown in Figure 8 (a). The most of the visual field is covered by amorphous phase in which a small quantity of crystalline is distributed. The additive caused the reducing amorphous phase from 80% to 60% and the growing crystalline to large host grains as shown in Figure 8 (b), so the EEB is increased by 8–11%.

Conclusions

It was confirmed by the experimental results that the VMC can be enriched into a designed mineral phase such as Perovskite for titania and Susanite for borate by proper operation factors like the slag composition and so on. During the solidification of the molten slags, the precipitating behavior of VMC could be artificially controlled by proper operation conditions like temperature of heat-treatment, cooling rate, and additives so as to approach the selective coarsening of Perovskite in Ti-slag and Saunite in B-slag.

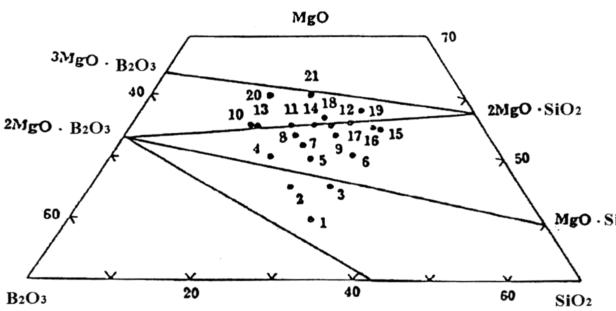
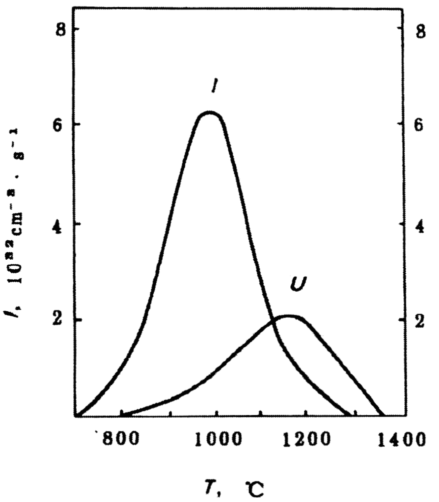
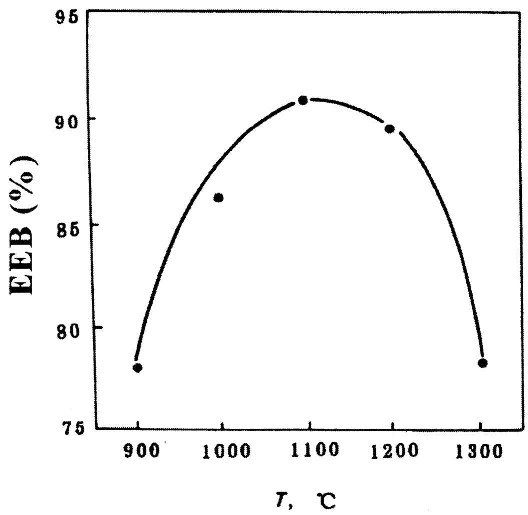


Figure 6. Composition of MgO-B_2O_3-SiO_2 system



(a) Calculated results



(b) Experimental results

Figure 7. Effect of heat treatment temperature on I-U and EEB

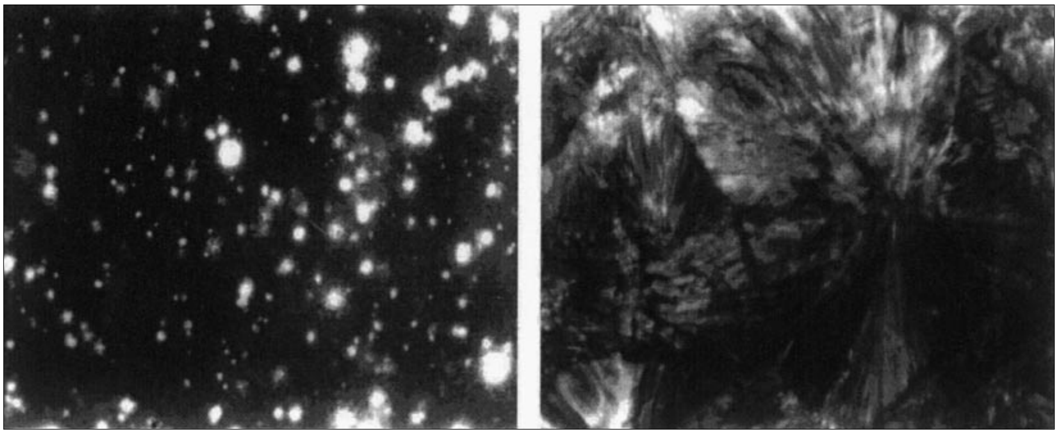


Figure 8. Micrographs of B-Slag samples treated without (a) and with (b) additive

The goal of separating the grown mineral phases from tailings can be fulfilled by dressing or hydrometallurgical process. These facts may come to the conclusion that the recovering VMC from the associated slags by SPT is available.

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