PN-ACK-381

Physico-chemical properties of matte – slag melts taken from Vanyukov's furnace for copper extraction

S.E.Vaisburd, D.G.Brandon (Technion, Israel)
S.M.Kozhakhmetov, E.B.Kenzhaliev (IMiO, Kazakhstan)

The properties of liquid slag and matte were studied in the autogeneous extraction of copper that occurs in a furnace of special construction, Vanyukov's furnace, (Kazakhstan). The density and surface tension of the melts were measured using the maximum bubble pressure method and the viscosity of the melts was measured by the rotational method.

These properties were determined in the temperature interval 1350 to 1550°C. The data derived were compatible with published slag and matte properties for melts in traditional metallurgical processes. The temperature coefficients of the surface tension, density and viscosity were determined and the technological significance of the results is considered.

Experimental Methods

The density and surface tension of the slag and matte melts were measured by the maximum bubble pressure method, and the viscosity of the slag was measured by the rotational method. All measurements were made on an experimental unit developed at the Technion – Israel Institute of Technology, Haifa. The experimental unit and measurement procedures have been described in detail previously [1].

Calibration of the high temperature viscometer was based initially on measurements made on a borax melt, while later calibrations were made using a ternary eutectic in the system CaO-Al_2O_3-SiO_2 (point 5, the anorthite glass eutectic) [2]. The results of calibration, including the present measurements, are presented in fig.1. The excellent agreement for all results obtained over a period of several years testifies the reliability of the calibration.

The alumina capillary used for surface tension and density measurements had an inner diameter 1.02 mm ground to a knife edge [1]. Measurements were made in the temperature range1350 to 1550°C for the slag, and in the range 1350 to 1500°C for the matte. The estimated accuracy of these measurements was: ±3% for surface tension, ±1% for density, and ±8% for viscosity.

Sample Preparation

Samples were obtained from Vanyukov's furnace in the Balkhash copper-smelting plant (BGMK), where an autogeneous process for sulphide ores is in operation using a furnace of special construction [3].

The chemical analysis of these samples is given in Table I. The symbol Fe^{II} indicates divalent iron, either in the slag (ferrous oxide, FeO) or in matte (iron sulphide, FeS).

The slag samples contained matte inclusions. The viscosity measurements require Newtonian liquid behavior, so the matte inclusions must be separated from the slag melt. The slag sample was melted in an electric furnace, when the inclusions separated to the surface and could be removed from the crucible as a scum. The refined slag was then crushed after cooling and used for measurements. The same procedure was used for the matte samples in order to remove slag inclusions.

Experimental Results.

The results are presented in Tables II to IV, and figs.2 and 3. However, the matte viscosity cannot be measured by the rotational method used for slag, since both metal and matte melts are characterized by very low viscosities. For this case the torsional oscillation method for viscosity measurements should be used [4]. However the kinematic viscosity values for the matte could be estimated from reference data [4] and these values are shown in Table V.

The following symbols are used in the Tables : [RD] – viscometer reading, η – dynamic viscosity, ν – kinematic viscosity, ρ – density, σ – surface tension, E –activation energy for viscous flow, P_m – maximum bubble pressure, h – depth of capillary submersion in the melt, n – number of measurements. The asterisk * signifies extrapolated values for 1300°C.

Discussion.

The temperature dependence of the surface tension and density is labelled $d\sigma/dT$ and $d\rho/dT$, respectively. The data show the expected linear dependence in both cases: For the slag $d\sigma/dT = +0.11$ mN/(m.K), and $d\rho/dT = -0.13.10^{-3}$ kg/(m^3.K); while for the matte $d\sigma/dT = +0.05$ mN/(m.K), $d\rho/dT = -0.06.10^{-3}$ kg/(m^3.K). The positive temperature coefficient of the surface tension for the slag is due to the break up of

silicate polyanions, which are surface-active in liquid slags [5]; the positive temperature coefficient of surface tension for the matte is associated with adsorption of sulphur in the surface layer. Sulphur is surface-active in sulphide melts but desegregates as the temperature increases [4]. The negative temperature coefficient of the density for both slag and matte is due to the increasing atomic separation at higher temperatures, Me-O in silicate melts and Me-S in sulphide melts [4,5].

The linear dependence of the graph for the logarithm of viscosity against reciprocal absolute temperature suggests Ahrrenius behavior with a unique activation energy. This activation energy for viscous flow, $E\eta$, defines the temperature dependence of the viscosity. For the slag $E\eta$ = +76.5 kJ/mol. The decrease in slag viscosity with increasing temperature is also associated with the dissociation of silicate polyions which control the viscous flow. The activation energy for the matte $E\nu$ = +28.3 kJ/mol also indicates a decrease in viscosity with increasing temperature due to the gradual breakdown of the Me-S bond in the sulphide melt [4].

The matte and slag melts studied here are complex, many-component systems, so the measured data cannot be compared accurately with any known reference data [4,6]. However, values obtained for the measured properties are comparable to other values for the properties of liquid matte and slag found in traditional metallurgical extraction processes [8,9].

It is of some practical importance to consider the technological implications of the present data.

The matte viscosity is reported here as a kinematic viscosity, as is usual for metal or matte liquids. The dynamic viscosity can be derived from the density values; to yield a value for 1300^0C of only 0.03 Pa.s. The slag viscosity (0.3 Pa.s) is also very low, so that both melts are removed easily from the furnace.

The matte density exceeds the slag density by $1.4\text{-}1.5\times10^3$ kg/m^3, thus ensuring effective sedimentation of matte regulae in the liquid slag. The low slag viscosity also promotes sedimentation of matte regulae. The inter-phase tension between slag and matte should also have an influence on the aggregation and coalescence of the regulae, with an increase in inter-phase tension leading to more effective coalescence. The inter-phase tension depends on the surface tension of the two phases. The higher the surface tension of the matte the greater the inter-phase tension, and the lower the surface tension of the slag the greater the inter-phase tension [4]. According to the

present data for surface tension of the components, the inter-phase tension is about 90-110 mN/m [8], sufficient to ensure effective coalescence.

It follows that the physico-chemical properties of the matte and slag melts are appropriate for the present metallurgical process.

Conclusions.

1. Physico-chemical properties of liquid slag and matte in the autogeneous Vanyukov's process were studied by taking samples from Vanyukov's furnace at the Balkhash copper-smelting plant (Kazakhstan).
2. The surface tension and density of melts were measured by the maximum bubble pressure method, while the viscosity of the slag was measured by the rotational method. All measurements were made on the experimental unit developed at the Technion – Israel Institute of Technology.
3. All the data obtained are comparable to those reported for industrial melts in traditional metallurgic processes.
4. The temperature coefficients of surface tension and density, and the activation energy for viscous flow were calculated, and the temperature dependence of slag and matte melt properties are analyzed.
5. The technological significance of these data for the physico-chemical properties of matte and slag melts is discussed.

Acknowledgments.

The authors acknowledge financial support for this investigation from the U.S. Agency For International Development under grant TA-MOU-98-CA17-017, included in the USAID Cooperative Development Research Program.

References.

1. S.Vaisburd and D.G.Brandon: *Meas. Sci. Technol.*, 1997, vol. 8, pp. 822-6.

2. E.M.Levin, C.R.Robbins and H.F.McMurdie: *Phase diagrams for ceramics*, 4-st Edition, The Amer. Ceram. Soc., Columbus, Ohio, 1979, pp.663-6.

3. *Smelting in Matte-Slag Liquid Emulsion*, Edited by A.V.Vanyukov, "Metallurgiya", Moscow, 1988, pp. 11-17. (russ).

4. S.E.Vaisburd: *Physico-chemical properties and specific features of the structure of sulfide melts* , "Metallurgy", Moscow, 1996, pp. 139-41; 165-8; 173-80; 189-91. (russ).

5. O.A.Yessin and P.V.Gueld: *Physical Chemistry of Pyrometallurgical Processes, part 2, Interactions with Participation of Melts*, "Metallurgiya", Moscow, 1966, pp. 223-9; 244-7. (russ.)

6. *Slag Atlas*, Verlag Stahleisen GmbH, D-Dusseldorf, 1995, pp. 328-41; 364-81; 430-49.

7. J.F.Elliott, M.Gleiser and V.Ramakrishna: *Thermochemistry for Steelmaking*, Reading, Massachusetts – London, 1963, pp. 239-40.

8. A.V.Vanyukov and V.Ya.Zaytsev: *Slags and Mattes of Non-Ferrous Metallurgy*, "Metallurgiya", Moscow, 1969, pp. 138-56. (russ.)

9. A.V.Vanyukukov and V.Ya.Zaytsev: *Theory of Pyrometallurgical Processes*, "Metallurgiya", Moscow, 1973, pp. 153-67. (russ).

Table I. Composition of melt products from Vanyukov's furnace (wt%)

Sample	Cu	Fe^{II}	S	CaO	SiO_2	Fe_3O_4	Al_2O_3	Zn	Pb
waste slag	0.31	32.40	1.90	2.90	33.80	3.20	5.10	6.3	1.20
matte	48.9	16.48	22.12	0.12	1.3		1.35	3.60	2.50

Table II. Viscosity of the waste slag.

t (^{0}C)	T (^{0}K)	1000/T	[RD].10^{-3}	η (Pa.s)	log η
1300	1573	0.636		0.31*	-0.509*
1350	1623	0.616	4.06	0.26	-0.585
1400	1673	0.598	3.47	0.22	-0.658
1450	1723	0.580	3.02	0.19	-0.721
1500	1773	0.564	2.56	0.16	-0.796
1550	1823	0.549	2.18	0.14	-0.853

Table III. Surface tension of the waste slag and matte.

t (°C)	T (°K)	slag			matte		
		n	P_m (mm H_2O)	σ (mN/m)	n	P_m (mm H_2O)	σ (mN/m)
1300	1573			359*			340*
1350	1623	3	145.6±1.7	364	3	136.8±1.2	342
1400	1673	4	148.0±1.3	370	3	138.0±1.5	345
1450	1723	4	150.0±1.8	375	4	138.8±1.8	347
1500	1773	5	152.8±1.9	382	4	139.6±1.7	349
1550	1823	5	154.8±1.8	387			

Table V. Kinematic viscosity of matte.

t (°C)	T (°K)	1000/T	ν (m^2/s)	log ν
1300	1573	0.636	6.3	0.800
1350	1623	0.616	6.1	0.782
1400	1673	0.598	5.8	0.764
1450	1723	0.580	5.6	0.746
1500	1773	0.564	5.3	0.729

Table IV. Density of the waste slag and matte.

t (°C)	T (°K)	h (mm)	slag				matte			
			n	P_m (mm H_2O)	ΔP_m (mm H_2O)	$\rho \cdot 10^{-3}$ (kg/m^3)	n	P_m (mm H_2O)	ΔP_m (mm H_2O)	$\rho \cdot 10^{-3}$ (kg/m^3)
1300	1573					3.34*				4.74*
1350	1623	3.0	4	155.4 ± 0.6	9.80	3.27	3	150.9 ± 0.5	14.13	4.71
		6.0	3	165.3 ± 0.6			3	165.1 ± 0.7		
		9.0	3	175.0 ± 0.6			3	179.2 ± 0.6		
1400	1673	3.0	4	157.6 ± 0.5	9.63	3.21	4	152.0 ± 0.6	14.03	4.68
		6.0	3	167.2 ± 0.5			3	166.1 ± 0.6		
		9.0	3	176.9 ± 0.6			3	180.1 ± 0.7		
1450	1723	3.0	4	159.4 ± 0.7	9.43	3.14	4	152.8 ± 0.6	13.97	4.66
		6.0	4	168.9 ± 0.6			3	166.7 ± 0.8		
		9.0	3	178.3 ± 0.8			3	180.7 ± 0.8		
1500	1773	3.0	4	162.1 ± 0.5	9.23	3.08	4	153.5 ± 0.7	13.90	
		6.0	4	171.5 ± 0.4			4	167.5 ± 0.8		
		9.0	3	180.8 ± 0.6			3	181.3 ± 0.7		
1550	1823	3.0	4	163.8 ± 0.6	9.05	3.02				
		6.0	4	172.9 ± 0.5						

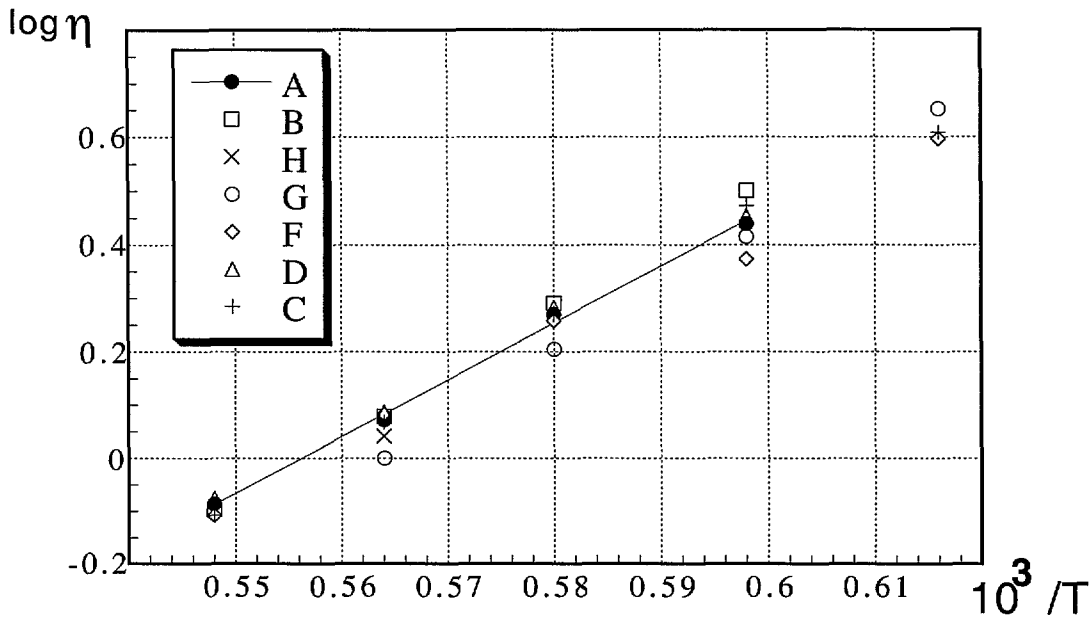

Fig.1 .Calibration of the high temperature viscometer. A – present measurements (2000). Previous measurements: B –(1994); C –(1996); D –(1998); F –(1999). Reference data: G – [6]; H – [7].

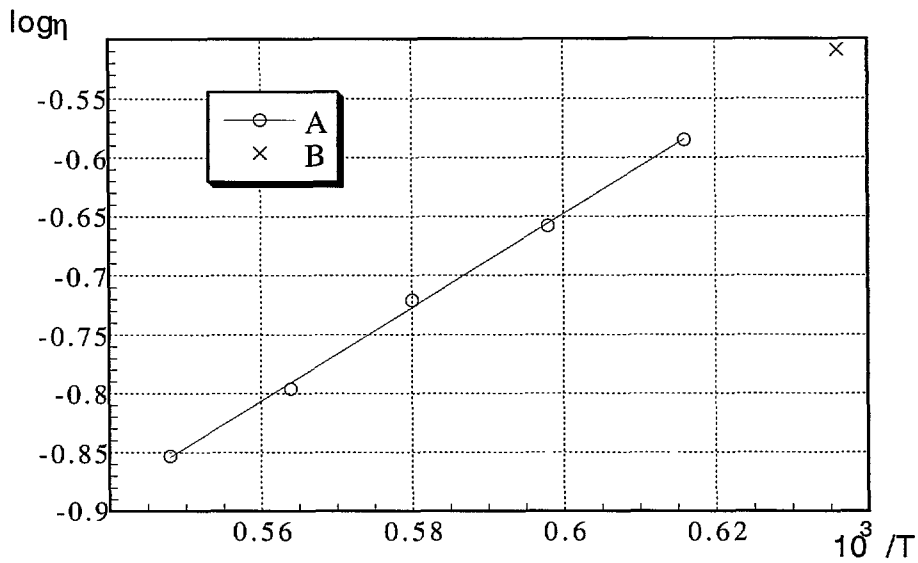

Fig.2. Viscosity of the waste slag. A – measured values,
B – value extrapolated to 1300°C.

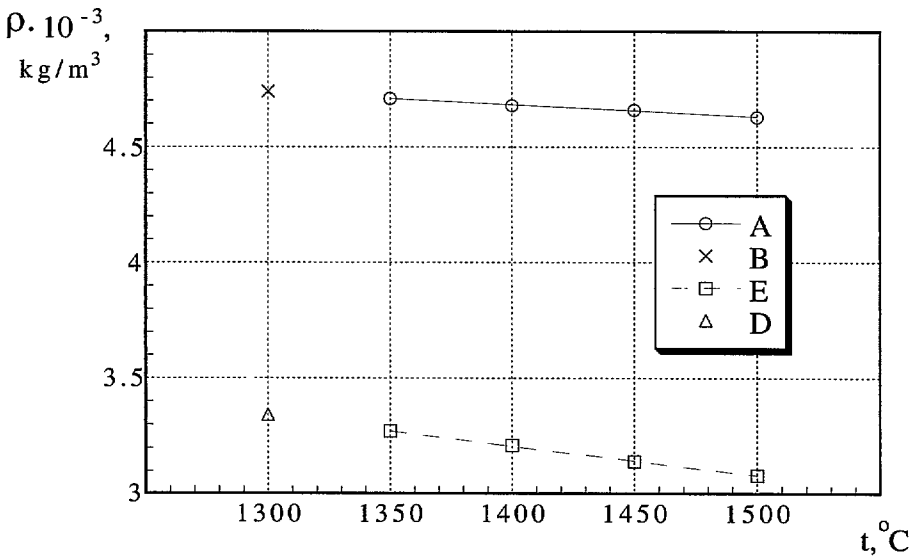

Fig.3. Density of the waste slag and matte. Experimental data: A – slag, E – matte. Data extrapolated to 1300°C: B – slag, D – matte.

Figure captions

Fig.1.
Calibration of the high temperature viscometer.
A - present measurements (2000); Previous measurements: B –(1994); C –(1996); D –(1998); F –(1999); Reference data: G – [6]; H – [7].

Fig.2.
Viscosity of the waste slag.
A – measured values, B – value extrapolated to 1300°C.

Fig.3.
Density of the waste slag and matte.
Experimental data: A – slag, E – matte; Data extrapolated to 1300°C: B – slag, D – matte.