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Viscosity of Spinel Primary Phase Field Slags from Australian Brown Coals

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ABSTRACT: The achievement of a steady rate of slag tapping in entrained-flow gasifiers relies on their continuous, smooth operation. In turn, this requires the viscosity of coal ash slags to be within 5–25 Pa·s at operating temperatures. However, slagging behavior, including viscosity, strongly depends on coal ash mineral and chemical composition. These vary significantly in Australian brown coal ashes, making continuous gasifier operation difficult. In our previous work, we identified brown coal ash compositions that satisfy entrained-flow gasification conditions and were attributed to specific primary phase fields of the corresponding slag compositions. In this work, we experimentally determined the viscosity and phase composition of slag samples prepared from the spinel primary phase field. On the basis of these results, we evaluated different viscosity models to identify those that accurately described the viscosity of the liquid phase. The models were then applied to describe the viscosity of two-phase slags with spinel crystals and evaluate effective slag viscosity. Lastly, we developed a model to describe the kinetics of spinel growth during slag isothermal crystallization and linked the model to the effective viscosity of the investigated slags.

1. INTRODUCTION

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Gasification of brown coals allows low-rank coals to be used in a more environmentally friendly manner. Entrained-flow gasification, which allows high throughput and flexibility in fuel feedstock, gives one an opportunity to process brown coals containing mineral matter with low-temperature slagging characteristics. These coals are not generally suitable for nonslagging gasification processes, such as fluidized-bed and fix-bed gasifiers. To process coals with relatively low ash melting temperatures (or low ash fusion temperatures), the molten coal mineral matter must form a protective slag layer on the gasifier walls.¹ The smooth operation of entrained-flow gasifiers also depends strongly on steady, reliable slag removal, which is reliant on slag flow behavior. To achieve steady slag tapping in entrained-flow gasifiers, one should form a constant thickness and consistent flow of the slag layer in order to protect refractory and minimize heat losses, and the viscosity of slags produced from bituminous and sub-bituminous coals should generally be within 5-25 Pa·s at operating temperatures of 1200-1500 °C.² These characteristics are based on the calculation of slag residence time in the gasifier and the amount of slag produced during coal gasification, which corresponds to a typical ash content in Australian high-rank coals of 5-15 wt %. The ash content in brown coals is significantly lower, typically 1-4 wt %,^{3,4} and the slags may need a longer residence time in the gasifier. Therefore, the slag viscosity value required to achieve a protective slag layer could be higher for brown coal than for high-rank coals. Slagging characteristics, particularly slag viscosity, strongly depend on coal mineral and chemical composition, which vary significantly in Australian brown coal ashes.^{4,5} As a result, the molten slags of Australian brown coal ashes represent various primary phase fields in a multicomponent system. In our earlier work

on slagging characteristics of brown coal ashes, we grouped them on the basis of the concentrations of major oxides, such as SiO₂, Al₂O₃, CaO, MgO, and Fe₂O₃.⁶ We found that some silica-rich and CaO-rich slags can be used unblended in entrained-flow gasifiers, while high-iron, high-magnesium, and some high-alumina slags could be used only in coal blends with high-silica coals. We also investigated the effect of sodium on slag viscosity,^{7,8} as the Na₂O concentration in brown coal ashes may exceed 10 wt % and could be considered as one of the major elements in ash composition. In these works, we found that sodium enrichment can significantly reduce slag viscosity to acceptable values but not for high-silica slags with very high viscosity. We also found that slags with very high viscosity represent compositions from the cristobalite and mullite primary phase fields. Another group of slags came from the olivine and cordierite primary phase fields and demonstrated slag viscosities in the range suitable for slag tapping.⁷ Slags from the spinel primary phase field with low silica/alumina weight ratio (S/A < 1) were found to have high liquidus temperatures and demonstrate non-Newtonian flow behavior.

In this work, we have extended the compositional range of brown coal slags with suitable slagging characteristics, such as liquidus temperatures below gasifier operating temperatures and viscosity values sufficient for slag tapping, to coal slags from the spinel primary phase field with S/A > 1. These coal

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Гabl	e 1.	Brown	Coal Ash	Compositions	(wt %)) Used	in	This	Stuc	ly
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sample	SiO ₂	Al_2O_3	Fe_2O_3	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO3	P_2O_5	Mn_3O_4	BaO	SrO
Bca11	41.7	25.7	5.7	3.25	5.4	6.01	1.32	1.19	9.70	0.09	0.04	0.08	0.05
Bca17	48.92	27.65	6.05	2.44	3.82	3.67	0.58	1.08	5.00	0.10	0.1	0.05	0.03
Bca20	51.25	22.50	7.30	1.84	4.26	4.80	0.39	0.95	5.11	0.06	0.1	0.04	0.04
Bca23	40.16	19.44	9.11	4.04	6.71	5.81	0.44	0.79	11.2	0.06	0.16	0.12	0.07
Bca27	26.1	19.2	6.5	4.81	9.4	8.8	0.35	0.63	21.8	0.07	0.07	0.15	0.09
Bca29	47.2	26.6	2.62	2.25	5.5	5.1	0.67	1.49	7.1	0.07	0.03	0.06	0.03

Table 2. Synthetic Slag Compositions (wt %) Corresponding to Brown Coal Ashes Listed in Table 1^a

ash	slag	SiO ₂	Al_2O_3	Fe_2O_3	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	S/A
Bca11	s11-1	46.39	28.59	5.93	3.62	6.01	6.69	1.47	1.32	1.62
Bca11n	s11-2	48.03	29.60	6.14	3.75	6.22	3.37	1.52	1.37	1.62
Bca17	s17-1	51.93	29.35	6.41	2.59	4.06	3.9	0.62	1.15	1.77
Bca17n1	s17-2	49.75	28.12	6.14	2.48	3.89	7.8	0.59	1.1	1.77
Bca17n2	s17-3	48.1	27.19	5.94	2.4	3.76	10.96	0.57	1.06	1.77
Bca20	s20-1	54.94	24.12	7.83	1.97	4.57	5.15	0.42	1.02	2.28
Bca20n	s20-2	52.12	22.88	7.43	1.87	4.34	10	0.4	0.97	2.28
Bca23	s23-1	46.43	22.48	10.53	4.67	7.76	6.72	0.51	0.91	2.07
Bca23n1	s23-2	48.09	23.29	10.91	4.84	8.04	3.37	0.53	0.94	2.06
Bca23n2	s23-3	44.8	21.69	10.16	4.51	7.49	9.99	0.49	0.88	2.07
Bca-27	s27-1	34.37	25.29	8.56	6.33	12.38	11.59	0.46	0.83	1.36
Bca27n	s27-2	36.67	26.98	9.33	6.75	13.21	5.85	0.49	0.89	1.36
Bca-29	s29-1	51.57	29.06	2.86	2.46	9.13	5.57	0.73	1.63	1.77
Bca29n	s29-2	48.58	27.38	2.69	2.32	5.66	11.14	0.69	1.54	1.77
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^{*a*}Ashes with modified Na₂O are marked with "n".

ash compositions were found in Loy Yang coal ashes, which have SiO_2 , Al_2O_3 , CaO, MgO, Na₂O, and Fe₂O₃ as major oxides (with concentrations within 5–50 wt %) and TiO₂ and K₂O as minor elements (with concentrations <2 wt %). Sulfur content is also high in brown coal ashes but does not appear in the slag under gasification conditions.

On the basis of the experimental results for slag viscosity, we then explored and evaluated different approaches to slag viscosity modeling. We have previously found that even small changes of sodium in ash chemistry may have a significant effect on slag viscosity and slag phase compositions.⁸ To assist with the development of a slag viscosity model, we considered the effect of sodium by varying sodium concentration in the slags. The effect of solids was also investigated for slag compositions where the solids concentration does not exceed a critical value (to transfer slag flow to non-Newtonian behavior) and allows slag tapping at temperatures below the liquidus temperature. The kinetics of spinel growth with isothermal crystallization were also considered and included in the viscosity model of partially crystallized slags.

2. EXPERIMENTAL SECTION

2.1. Ash Preparation. Brown coal samples were crushed to a 4 mm size and placed in alumina boats. Samples were then heated to 250 $^{\circ}$ C in a muffle furnace and kept for 1 h before the temperature was increased to 780 $^{\circ}$ C. Samples were kept at 780 $^{\circ}$ C for 20 h followed by a slow cooling process.

2.2. Slag Preparation. Due to the low ash content of the investigated brown coals, slag samples were prepared to reproduce bulk compositions of the ashes obtained in the present study by mixing laboratory or analytical grade Al_2O_3 , CaO, Fe₂O₃, K₂CO₃, MgO, Na₂CO₃, SiO₂, and TiO₂ powders. Alkali carbonates were used in initial mixtures as they transfer to oxides at high temperatures. The mixtures were pelletized, placed in molybdenum (Mo) crucibles, premelted at 1500–1600 °C in a neutral atmosphere (N₂), and then

kept at this temperature for 4–5 h before commencing slag viscosity measurements. To ensure the reducing atmosphere, the crucible was placed in a sacrificial graphite liner. Oxygen partial pressure (pO₂) in the system was measured separately using an oxygen probe (HT oxygen probe, Australian Oxytrol Systems). At temperatures between 1200 and 1450 °C, pO₂ values near the slag surface were between 2.8 \times 10⁻¹¹ and 2.9 \times 10⁻⁹ atm.⁹

To investigate the effect of sodium in prepared slags and to obtain slag composition in the spinel primary phase field, each parent slag composition was enriched or reduced in sodium oxide concentration. The composition of these synthetic slags also consists of eight major oxides, where only Na₂O concentration is variable.

Slag samples for subsequent compositional and microstructural analysis were obtained after viscosity measurements by cold rod quenching at a fixed temperature as previously described.⁹

2.3. Viscosity Measurements. Slag viscosity was measured using a Haake high-temperature viscometer with a rotational bob technique described previously.^{2,9} Viscosity was measured at different shear rates using a Mo rotating sensor through the heating process up to the highest temperature (1600 °C) and then in the cooling cycle in 25-50 °C steps at temperatures of 1200–1600 °C. The temperature was then kept constant for at least 30 min to enable the slag to reach equilibrium before the measurement commenced. In the slag subliquidus temperature range, the slag was kept for a much longer time (1-3 h) to observe the kinetics of solids and viscosity growth. At each temperature point, slag viscosity was measured several times to ensure repeatability, and the average of these measurements was used as the value of the viscosity. The accuracy of the temperature measurements was within ± 2 °C. The standard deviation of the measurements was below 2%, which is less than the overall uncertainty of the measurements.

At certain temperatures, quenched slag samples were obtained directly after viscosity measurements.

2.4. Sample Analysis. Bulk compositions of ashes determined by X-ray fluorescence according to the ASTM D3174-12 standard are listed in Table 1. For major elements, the uncertainty in XRF results is within 0.5-1%. The compositions of synthetic slags were recalculated on a sulfur-free base without minor elements, such as MnO₃, SrO, and



Figure 1. Calculated slag phase compositions

BaO (as their concentrations are less than 0.2 wt %) and are listed in Table 2. Sulfur is almost absent in gasification slags, because it appears in gaseous form under gasification conditions.⁶

Quenched slags obtained during viscosity tests were examined using scanning electron microscopy (SEM) in the electron backscattering mode. The sample microstructures and the phase compositions were determined using a JEOL 8800L Electron Probe Microanalyzer (EPMA) with wavelength dispersive detectors (WDDs), an accelerating voltage of 15 kV, and a probe current of 15 nA. Phase compositions of ashes and slags were also calculated using the FactSage (version 7.1) thermodynamic phase equilibria package with FactPC and FToxid databases selected for slag, solid solutions, and compounds.¹⁰

3. RESULTS AND DISCUSSION

3.1. Slags Microstructure and Phase Composition. According to thermodynamic calculations, most of the investigated slags appeared in the spinel primary phase field, as illustrated in Figure 1. Slags s11-1 that corresponded to Bca11 ash belonged to the spinel (Fe,Mg)Al₂O₄ primary phase field, and secondary phase feldspar (CaAl₂Si₂O₈) formed at lower temperatures. When sodium content in this ash is halved, the corresponding slag composition moved to the mullite primary phase field and spinel appeared as a secondary phase. Reducing temperatures to 1200 °C led to the formation







Figure 2. Microstructure of quenched slags: (a) s11-1 ($T_q = 1250 \text{ °C}$), (b) s11-2 ($T_q = 1350 \text{ °C}$), (c) s17-1 ($T_q = 1425 \text{ °C}$), (d) s17-2 ($T_q = 1275 \text{ °C}$), (e) s17-3 ($T_q = 1200 \text{ °C}$), (f) s20-1 ($T_q = 1200 \text{ °C}$). Legend: L, former liquid phase; Sp, spinel ((Fe,Mg)Al₂O₄); M, mullite (3Al₂O₃·2SiO₂).

of other phases, such as sapphirine, cordierite, and feldspar as well as a slight increase of the predicted liquidus temperature, $T_{\rm liq}$. The microstructure of quenched slags s11-1 and s11-2 (Figure 2a,b, respectively) showed that both have only one

solid phase at 1250 and 1350 °C, respectively. EPMA analysis revealed that the composition of the solid phase was close to stoichiometry $Fe_{0.15}Mg_{0.85}Al_2O_4$, which can be identified as the spinel phase (Fe,Mg)Al₂O₄.



Figure 3. Microstructure of quenched slags: (a) s23-1 ($T_q = 1200 \text{ °C}$), (b) s23-2 ($T_q = 1250 \text{ °C}$), (c) s27-1 ($T_q = 1235 \text{ °C}$), (d) s27-2 ($T_q = 1200 \text{ °C}$), (e) s29-1 ($T_q = 1275 \text{ °C}$), and (f) s29-2 ($T_q = 1225 \text{ °C}$). Legend: L, former liquid phase; Sp, spinel ((Fe,Mg)Al₂O₄); M, mullite (3Al₂O₃· 2SiO₂); Ol, olivine ((Mg,Fe)₂SiO₄).

Slag that reproduced the Bca17 composition (s17-1) was expected to be in the mullite primary phase field (Figure 1b) with $T_{\text{liq}} = 1443 \text{ °C}$, and this was confirmed by the microstructure of s17-1 slag quenched from 1425 °C (Figure

2c). At lower temperatures, cordierite and feldspar appeared as secondary phases according to phase equilibria calculations. When the ash composition was enriched with Na_2O from 3.9 to 7.8 wt %, the slag primary phase field moved to the spinel



Figure 4. Viscosity of slags versus temperature for Bca11 (a), Bca17 (b), Bca20 (c), Bca23 (d), Bca27 (e), and Bca29 (f). Thin and thick dashed lines show 5 and 25 Pa·s viscosity values, respectively. Arrows indicate calculated slag liquidus temperature (see Figure 1).

primary phase field, significantly lowering T_{liq} to 1330 °C. The corresponding quenched slag microstructure (at 1225 °C, Figure 2d) supports the thermodynamic calculations. Further Na₂O enrichment (up to 11 wt %) did not decrease calculated T_{liq} (1132 °C) but lowered the spinel content at the same temperatures. The quenched s17-3 slag also had only spinel crystals at 1200 °C (Figure 2e).

Slag representing Bca20 ash (s20-1) was expected to be in the cordierite primary phase field, and the cordierite phase is the only one in equilibrium with the liquid phase at temperatures above 1200 °C and below $T_{\text{liq}} = 1309$ °C according to FactSage calculations. However, the microstructure of the s20-1 slag quenched from 1200 °C consisted only of liquid phase with spinel. When Na₂O concentration increased from 5 to 10 wt %, $T_{\rm liq}$ decreased significantly to 1236 °C. However, no solids were detected in the s20-2 sample quenched from 1200 °C, as only 1.6 wt % of spinel is expected in this slag at this temperature according to thermodynamic calculations. There may have not been enough time in the experiment to precipitate such small amounts, or the crystalline phases may be too small to be observed.

The composition of slags representing Bca23 ash lay in the spinel primary phase field, and its $T_{\rm liq} = 1303$ °C according to FactSage calculations. The slag sample s23-1 with an Na₂O concentration of 6.7 wt % quenched from 1200 °C (Figure 3a) had a liquid phase with spinel only. Lowering the Na₂O

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Table 3. Phase Composition (wt %) of Quenched Slags

$T_{\text{quench'}}$ °C	phase	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MoO_3
				s11-	-1 (Bca11)					
1300	glass	47.99	28.11	5.55	3.42	5.22	6.65	1.36	1.43	0.4
1290	glass	51.15	25.37	5.63	3.34	4.12	6.71	1.43	1.45	0.44
	spinel	0.1	66.17	10.43	0	21.72	0	0	0.16	1.7
1280	glass	51.94	24.9	5.57	3.46	3.89	6.64	1.47	1.48	0.31
	spinel	0.1	65.2	11	0	21.2	0	0	0.2	2.8
1270	glass	52.26	24.75	5.56	3.42	3.8	6.66	1.47	1.48	0.37
	spinel	0	66.35	11.11	0	21.45	0	0	0.19	1.21
1260	glass	53.02	24.77	4.94	3.7	3.69	6.92	1.53	1.57	53.02
	spinel	0.15	65.36	11.3	0	20.41	0	0	0.21	0.15
1250	glass	53.61	25.25	5.44	3.82	3.54	6.48	1.63	1.53	0.35
	spinel	0.12	65.78	12.17	0	20.89	0	0	0.25	1.68
1550	alaaa	10 76	20.44	s11 6.05	2 (Bcalln)	617	2.4	1.52	1.26	0.2
1350	glass	40.20	29.44	5.00	5./ 2.42	5.04	5.4	1.55	1.50	0.5
1550	giass	0.01	20.88 68 74	0.03	0.01	20.73	4.1	0	0.14	1.2
1325	glass	517	26.73	9.93 4.78	3.1	5 15	3 99	1.67	1.31	0.3
1525	spinel	0.03	69.06	893	0.01	21.11	0	0	0.11	1.0
	spiner	0.05	07.00	s17-	-1 (Bca17)	21.11	0	0	0.11	1.0
1525	glass	52.33	29.88	6.15	2.36	3.75	3.62	0.74	1.13	1.09
1425	glass	52.56	29.49	6.11	2.41	3.81	3.71	0.77	1.12	1.01
	mullite	25.59	72.42	0.47	0	0	0	0	0.57	0.6
				s17-2	2 (Bca17n1)					
1300	glass	51.15	27.2	6.25	2.58	3.1	7.68	0.57	1.18	0.72
	spinel	0.19	64.69	15.66	0.03	18.06	0.03	0.03	0.16	2.67
1225	glass	51.64	26.76	6.14	2.65	2.92	7.62	0.55	1.22	1
	spinel	1.51	62.24	15.97	0.08	17.58	0.19	0.04	0.17	3.93
				s17-3	8 (Bca17n2)					
1300	glass	49.6	26.4	6.1	2.5	3.0	10.2	0.6	1.1	0.6
1200	glass	50.3	27.88	5.68	2.45	3.41	8.94	0.54	1.23	50.3
	spinel	0.05	65.53	12.47	0.02	20.55	0	0	0.13	0.05
1000	1	54.05	aa o a	s20-	-1 (Bca20)		5.95		0.07	0.05
1200	glass	56.05	22.92	7.91	1.95	3.73	5.35	0.4	0.97	0.95
	spinel	0.3	64.93	15.45	0.04	18.31	0.06	0.02	0.17	2.0
1200	alass	53 34	23 43	7.81	1 (Dea2011)	375	8 4 1	0.4	1.08	0.73
1200	51455	55.51	20.10	\$23	-1 (Bca23)	5.75	0.11	0.1	1.00	0.75
1250	glass	46.49	21.55	10.68	4.46	6.52	7.35	0.49	0.88	1.43
1200	glass	46.89	21.72	10.68	4.53	6.55	7.42	0.49	0.89	1.23
	0			s23-2	2 (Bca23n1)					
1500	glass	47.34	22.94	9.3	4.19	7.47	3.69	0.56	0.96	2.29
1300	glass	47.51	23.09	9.48	4.23	7.58	3.64	0.6	0.95	1.72
	spinel	0.1	65.51	12.2	0	20.63	0	0	0.1	0.3
1275	glass	48.86	22.1	9.49	4.36	7.24	3.79	0.5	0.99	1.38
	spinel	0	65.5	12.11	0	20.78	0	0	0.1	0.27
1250	glass	49.57	21.31	9.23	4.46	7.1	4.4	0.5	1.04	0.95
	spinel	0.1	65.28	12.18	0	20.45	0	0	0.1	0.4
1225	glass	50.45	20.77	9.27	4.56	6.87	4.27	0.6	1.03	0.7
	spinel	0.1	65.53	12.47	0	20.55	0	0	0.1	0.1
4000	,	45.00		s23-3	6 (Bca23n2)	(0.40		
1300	glass	45.09	20.90	10.36	4.33	6.32	10.20	0.48	0.85	0.9
1200	glass	46.26	22.27	4.15	9.42	6.88	9.78	0.51	0.89	1.1
	spinei	0.1	03.38	12.1/	$(B_{c2}27)$	20.55	U	U	0.1	0.4
1540	olass	35 72	26.13	8 3 9	5.76	12,19	10.16	0.46	0.87	1.52
1300	glass	37.08	23.6	8.92	5.98	11.13	11.84	0.48	0.9	1.52
	spinel	0.41	62.87	6.56	0	25.21	0	0	0.76	4.09
1275	glass	39.72	20.33	8.99	6.49	10.05	12.55	0.53	0.95	1.82
-	spinel	0.41	62.87	6.56	0	25.21	0	0	0.76	4.09
1250	glass	40.26	19.94	8.99	6.53	10.03	12.61	0.52	0.96	1.69
	spinel	0.29	65.03	6.64	0	25.61	0	0	0.52	2.69

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phase	SiO ₂	Al_2O_3	Fe_2O_3	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MoO_3
			s27	-1 (Bca27)					
glass	40.58	20.72	9.24	6.62	8.56	13.12	0.58	1.02	1.06
spinel	0.47	63.34	6.73	0	25.22	0	0	0.83	3.68
olivine	40.33	1.78	8.86	0.68	50.39	0	0	0	0
			s27-	2 (Bca27n)					
glass	43.71	20.2	9.33	7.43	8.93	6.61	0.58	1.03	1.93
spinel	0.13	62.04	8.51	0	22.61	0	0	0.17	5.86
glass	44.52	20.32	9.05	7.91	6.82	7.46	0.58	1.09	2.59
spinel	0	64.99	9.04	0	23.21	0	0	0.17	3.98
olivine	40.48	0.25	13.78	0.35	47.59	0	0	0	0
			s29	-1 (Bca29)					
glass	53.25	27.64	3	2.31	4.93	5.66	0.73	1.66	0.63
glass	56.19	25.29	2.88	2.42	4.27	5.72	0.76	1.73	0.49
spinel	0	63.95	9.12	0	23.2	0	0	0.15	3.98
mullite	23.88	70.5	1.21	0	0	0	0	0	0.41
			s29-	2 (Bca29n)					
glass	50.9	27.4	2.71	2.23	4.48	9.92	0.67	1.65	0.98
spinel	0.57	63.79	5.66	0	23.55	0	0	0.21	5.68
	els inued phase glass spinel olivine glass spinel olivine glass spinel olivine glass spinel mullite glass spinel	els inued phase SiO ₂ glass 40.58 spinel 0.47 olivine 40.33 glass 43.71 spinel 0.13 glass 44.52 spinel 0 olivine 40.48 glass 53.25 glass 56.19 spinel 0 mullite 23.88 glass 50.9 spinel 0.57	glass 40.58 20.72 spinel 0.47 63.34 olivine 40.33 1.78 glass 43.71 20.2 spinel 0.13 62.04 glass 44.52 20.32 spinel 0 64.99 olivine 40.48 0.25 glass 53.25 27.64 glass 56.19 25.29 spinel 0 63.95 mullite 23.88 70.5 glass 50.9 27.4 spinel 0.57 63.79	els sinued phase SiO ₂ Al ₂ O ₃ Fe ₂ O ₃ glass 40.58 20.72 9.24 spinel 0.47 63.34 6.73 olivine 40.33 1.78 8.86 c spinel 0.13 62.04 8.51 glass 43.71 20.2 9.33 9.05 spinel 0.13 62.04 8.51 glass 44.52 20.32 9.05 spinel 0 64.99 9.04 01vine 40.48 0.25 13.78 glass 53.25 27.64 3 3 3 glass 56.19 25.29 2.88 3 3 glass 56.19 25.29 2.88 3 3 spinel 0 63.95 9.12 3 mullite 23.88 70.5 1.21 229 glass 50.9 27.4 2.71 3 spinel <t< td=""><td>els pubs.acs.org inued 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0 0.17 glass 53.25 27.64 3 2.31 4.93 5.66 0.73 1.66 glass<

concentration to 3.4 wt % increased the liquidus temperature of the slag to 1319 °C, and two more phases were expected from phase equilibria calculations: cordierite at temperatures below 1270 °C and feldspar at temperatures below 1220 °C. However, only spinel solid phase was observed in slag s23-2 quenched from 1250 °C (Figure 3b) and 1225 °C. A much longer time is probably required to observe cordierite phase formation at these temperatures. When Na₂O concentration was 10 wt %, $T_{\rm liq}$ decreased to 1256 °C and spinel content decreased accordingly, with only 1.9 wt % expected by phase equilibria. Similar to s20-2 slag, the solid concentration was insufficient to be observed in slag s23-3 quenched from 1200 °C.

Relatively high sodium (11.5 wt %) slag s27-1, representing Bca27 ash, was found to be in the spinel primary phase. Despite its high liquidus temperature ($T_{\text{liq}} = 1519 \text{ °C}$), the concentration of spinel did not dramatically increase as the temperature fell from 1500 to 1200 °C. Only spinel crystals with former liquid phase were observed in sample s27-1 quenched from 1225 °C (Figure 3c). When Na₂O concentration decreased to 5.85 wt % in the paired slag sample s27-2, T_{liq} slightly increased to 1531 °C, and spinel growth was more dramatic as the temperature decreased. At temperatures lower than 1220 °C, olivine appeared as a second solid phase and was observed in sample s27-2 quenched from 1200 °C (Figure 3d), supporting the thermodynamic calculations.

The last pair of samples s29-1 and s29-2 corresponded to Bca29 ash with 5.6 and 11.1 wt % of Na₂O, respectively. Sodium enrichment (in slag s29-2) decreased T_{liq} from 1389 to 1361 °C according to FactSage calculations and significantly decreased the solids concentration at temperatures below the liquidus (Figure 1f). Only spinel crystals as solid phase were observed in sample s29-2 quenched from 1200 °C, supporting thermodynamic calculations. While slag s29-1 is expected to be in the mullite primary phase field, with other solids (sapphirine, cordierite, and feldspar) subsequently appearing when the temperature is reduced to 1200 °C, the real slag composition quenched from 1250 °C consisted of liquid phase, spinel crystals, and elongated mullite crystals (Figure 3e).

In general, most of the thermodynamic calculations agreed with the SEM observation of quenched slags. Some differences can be associated with the kinetics of solids growth and will be discussed in Sections 3.4 and 3.5, along with detailed EPMA analysis of slag microstructures, which enables the solid content to be estimated and compared with phase equilibria calculations.

3.2. Slag Viscosity and the Effect of Sodium. Figure 4 demonstrates that slag viscosity always decreased as sodium concentration rose in fully liquid slags. When solids started to affect slag viscosity, the viscosity of Na-enriched slag was also lower than slags with low sodium content, except for Bca27 slags. In sodium-enriched Bca27 slags, a sharp viscosity increase and non-Newtonian behavior was observed at 1225 $^{\circ}$ C, while in the low-sodium slag, this occurred at a lower temperature.

Most of the slags demonstrated Newtonian flow (linear shear stress-shear rate dependence) with viscosities between 5 and 25 Pa s at 1400–1550 $^\circ\text{C},$ which is desired for entrainedflow gasification. The corresponding temperature ranges were 1420-1570, 1450-1600, and 1300-1450 °C for slags representing Bca11, Bca17, and Bca23 coal ashes, respectively. The temperature range (corresponding to 5-25 Pa·s viscosity values) for Bca20 and Bca29 was relatively higher at 1500-1650 °C. The viscosity of these slags (s20-1 and s29-1) can probably be lowered by adding flux, such as CaO, as all these ashes have low CaO content. The viscosity values of sodiumenriched slags from these pairs (s20-2 and s29-2) were within 5–25 Pa·s at 1450–1600 °C. Slags representing Bca27 coal ash had a lower temperature range of 1250-1350 °C, suitable for slag tapping in entrained-flow gasifiers. These are the only slags with viscosity values between 5 and 25 Pa·s that correspond to the temperatures below their predicted liquidus temperatures. Therefore, solid precipitation and growth may significantly affect their viscosity. All other slag compositions have viscosity values within 5-25 Pa·s at temperatures above their predicted liauidus.

3.3. Modeling Viscosity of Fully Liquid Slag. As discussed previously, brown coal ash compositions can vary significantly. In the studied brown coal ashes, the concentrations of major elements, such as SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO are within a range of concentrations typical for Australian black coals. However, the viscosity models developed in the

Та	ıbl	e 4	. Eva	luation	of	Viscosity	Mo	dels	for	Fully	y Liquid	Coal	Ash	SI	lag
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	C1			A	verage 1	elative de	viation (%)		
Sample	Chem. comp.	Urbain [1]	K-I	F [2]	W- F ^[3]	Lakato $s^{[4]}$	T- shift ^[5]	K-J ^[6]	$FS^{(7)}$	
FeO, %		100	100	90	0	100	100	100	100	90
11.1	Table3	15.5	38.1	35.4	71.7	166.1	57.0	27.8	48.5	51.8
s11-1	Table2	33.4	52.2	50.1	80.4	141.0	68.5	22.8	3.7	5.0
11.0	Table3	22.1	40.6	37.9	70.2	214.4	56.7	32.9	5.9	5.7
s11-2	Table2	24.5	42.5	39.9	71.3	218.6	58.4	35.7	9.3	7.8
-17 1	Table3	15.8	12.3	9.7	37.9	367.2	23.7	37.7	46.0	46.8
s1/-1	Table2	14.4	18.0	14.2	45.9	253.5	38.4	32.7	45.0	46.4
-17.0	Table3	16.2	29.2	25.3	56.7	99.2	49.2	29.5	145.9	153.1
S1/-2	Table2	36.0	43.8	40.9	68.7	98.8	60.5	32.3	77.9	83.4
-17.2	Table3	29.1	43.3	40.1	68.2	67.3	60.1	32.7	175.6	185.8
\$17-5	Table2	48.0	57.4	55.3	79.5	59.2	71.1	32.5	94.1	101.0
s20-1	Table2	21.2	36.4	31.4	56.2	17.2	65.4	32.9	50.0	53.2
	Table3	12.5	34.4	29.0	54.7	52.9	63.5	33.3	135.2	145.8
\$20-2	Table2	31.7	53.6	50.0	72.4	44.5	74.4	34.0	74.0	82.0
c22 1	Table3	113.2	14.0	7.7	53.3	147.4	57.0	45.1	37.0	43.8
823-1	Table2	87.2	23.1	16.3	63.3	132.6	61.8	26.3	6.8	10.2
	Table3	140.3	14.9	25.0	33.9	240.6	40.3	22.7	45.0	50.7
823-2	Table2	117.0	6.7	5.4	44.7	207.8	52.9	17.2	3.6	5.5
c72.2	Table3	122.3	17.6	9.6	60.6	76.4	55.3	83.1	70.9	80.0
823-3	Table2	90.0	28.3	21.9	71.0	58.9	61.7	54.1	31.1	37.3
c27_1	Table3	126.7	8.8	12.0	89.2	127.4	54.7	83.4	4.2	4.2
527-1	Table2	103.6	12.7	9.1	93.1	23.3	64.4	67.4	21.9	19.6
s27-2	Table2	86.8	31.7	32.3	89.8	149.1	67.3	38.1	46.6	45.5
c20_1	Table3	38.3	44.7	43.3	73.7	41.6	54.2	21.9	52.5	54.3
347-1	Table2	70.5	75.9	75.4	91.7	28.4	84.7	49.6	54.8	54.3
s29-2	Table2	62.5	70.0	69.4	90.0	41.0	78.9	37.1	31.9	33.8
Average	Table3	63.6	28.5	26.5	63.2	123.3	54.8	41.2	72.1	77.5
Average	Table2	59.1	39.5	36.6	72.7	105.3	64.9	36.6	39.3	41.8

past decade for Australian black coals are not applicable to these ash compositions, as they also have significant concentrations of MgO (up to 13 wt % in the slags used in the present study) and Na₂O (up to 12 wt %). Due to the very wide range of slag compositions, it is hard to use only one model to calculate the viscosity of brown coal slags. In this study, we therefore evaluated different models (the original Urbain,¹¹ Kalmanovitch–Frank (K–F),¹² Watt–Fereday (W– F),¹³ Lakatos,¹⁴ T-shift,¹⁵ Kondratiev–Jak (K–J),¹⁶ and FactSage (FS)¹⁷) for their potential to calculate the viscosity of brown coal slags. The viscosity of fully liquid coal ash slag was evaluated by applying different viscosity models for fully liquid slag compositions, as determined by EPMA and listed in Table 3, and by comparing the calculated values with the experimental data.

The original Urbain,¹¹ K–J,¹⁶ Lakatos,¹⁴ and T-shift¹⁵ models were developed only for FeO-containing slags; therefore, all iron was taken as FeO in their calculations. W–F¹³ considered all iron to be Fe₂O₃; for this calculation, all iron was recalculated as Fe₂O₃. K–F¹² provided a general formula for both FeO- and Fe₂O₃-containing slags but optimized their model, taking all iron as FeO. FS¹⁷ can take into account both FeO- and Fe₂O₃-containing slags. Calculation results for these two models are presented for two cases: all iron was taken as (i) FeO or (ii) 90% FeO and 10% Fe₂O₃ (corresponding to our experimental conditions and partial oxygen pressure⁶). For each model, the viscosities were also recalculated using the bulk chemical compositions listed in Table 2 to check if the differences between slag chemical

compositions can significantly affect the calculated viscosity values.

On the basis of the model predictions, the viscosity models were ranked (see Table 4) using the average relative deviation calculated for each sample:

$$RD = \frac{1}{Np} \sum_{i=1}^{Np} \left| \frac{\eta_i^{calc} - \eta_i^{meas}}{\eta_i^{meas}} \right| \times 100\%$$
(1)

where η_i^{calc} is the viscosity calculated by a model and η_i^{meas} is the measured viscosity value for the *i*-th temperature (*Np* is the number of viscosity–temperature points). Deviations of more than 50% are shaded in Table 4.

Table 4 shows that, while FS was very sensitive to chemical composition, the other models did not dramatically differ in predictions, depending on whether the slag composition was taken from Table 3 or from Table 2.

The K–F model predicted the viscosity of slag reasonably well with a relative deviation of <50%. FS had a very good fit with the experimental data for particular slags but not all. The absence of Na₂O, which is high in the studied ash, limited the modified Urbain model to certain slag compositions. The inconsistency of viscosity predicted by the T-shift model, particularly for s23-2, s27-1, and s27-2, is caused by high MgO and Na₂O in the investigated slags, which are beyond the upper limit of these compounds in the model (Table 2).

The viscosity calculated by the original Urbain model was consistently lower than the experimental data for all slags due to high concentrations of CaO, K_2O , and Na_2O , which



Figure 5. Experimental and calculated viscosities of the Bca11 (a), Bca17 (b), Bca20 (c), Bca23 (d), Bca27 (e), and Bca29 (f) slags using the Kalmanovitch–Frank (K–F), Kondratiev–Jak (K–J), and FactSage (FS) models.

significantly reduced slag viscosity. W–F was suitable for the high SiO₂, CaO, and Fe₂O₃ slags but did not account for Na₂O, while the Lakatos model was mainly applicable for high-silica glasses without iron oxide. These caused a large deviation of their viscosities from the experimental data.

Figure 5a-f shows the experimental data and viscosities predicted by the K-F, K-J, and FS models. Both the K-F and FS models appeared to predict a correct slope of the log viscosity-temperature curves, while the K-J model predicted viscosity values close to the experimental data, but the calculated slope was lower than the experimental slope. In general, the K-F and FS models look to be the best for use in further modeling. Table 4 shows that the FS model had a very strong deviation in some cases (e.g., for s17-2 and s17-3),

while the K-F model demonstrated more consistent calculations for all investigated slags. This will also be discussed in the next section.

3.4. Application of Viscosity Model for Partially Crystallized Slag. Most slags with spinel crystals (up to 9 vol %) investigated in the present study demonstrate Newtonian flow behavior. One reason for this is the low spinel concentration, which does not increase dramatically as temperatures fall, as demonstrated in Figure 1. This provides an opportunity to apply experimental results to evaluate different viscosity models for solid–liquid suspensions demonstrating Newtonian flow.

Most viscosity models for a liquid with solids link slag viscosity with the viscosity of the residual liquid and volume



Figure 6. Spinel content and viscosity of partially crystallized s11-1 (a), s27-1 (b), and s23-2 (c) slags experimentally determined and predicted by the Kalmanovitch–Frank (K–F) and FactSage (FS) models.

fraction of the solids. In the present study, a set of quenched samples of s11-1, s23-1, and s27-1 slags were obtained to determine their solid content at specific temperatures for use as a parameter in the overall viscosity definition. This set of slags was obtained by holding samples at certain temperatures for a relatively long time (1.5-6 h depending on the temperature) to form the spinel phase out of the melt.

The weight fraction of crystalline phases was estimated from the EPMA data (Table 3) using the mass balances for 3–5 oxide components. The volume fraction of solids was then calculated using the density models of the liquid and spinel phases developed by Bottinga et al.¹⁸ and Niu and Batiza,¹⁹ respectively. The error was estimated from the standard deviations of the average values of the weight fractions of the solids.

Figure 6 shows the solid-phase content calculated by FactSage and measured experimentally over a range of temperatures and the corresponding experimental values of slag viscosities. The calculated viscosities of the liquid phase are also plotted to illustrate the effect of liquid-phase compositions on the increase in overall viscosity with the solid growth. The remaining viscosity change is then associated with the amount of solid phase.

To more accurately predict the viscosity of the residual liquid phase, we evaluated it in the following way. First, the initial values were predicted by the K–F and FS models using the liquid-phase composition from Table 3. Then, to adjust the model predictions, two correction coefficients were used: one for the slope correction and another for the up/down

adjustment. These coefficients were used to obtain a best fit to the experimental data of fully liquid slags. It was also assumed that the correction coefficients do not change when solids start to precipitate out and the liquid-phase composition changes accordingly. An example of such a correction is shown in Figure 7 for three selected slags (s11-1, s27-1, and s23-2), which shows that the liquid viscosities are well predicted by both models. The arrows in Figure 7 indicate the approximate beginning of crystallization, so only the liquid phase is present at higher temperatures (experimental points to the left of the arrow), while two-phase slag occurs at lower temperatures (points to the right of the arrow). The correction coefficients obtained in this way were then used to calculate viscosities of the remaining liquid phase at lower temperatures.

Figure 6 clearly shows that, as the temperature fell, the viscosity of the slags with crystallized solids increased more than that of the fully liquid slag. However, the contribution of solid content to the viscosity increase is different for the present slags. The s11-1 slag, in which viscosity is very high (100 s Pa·s below $T_{\rm liq}$), demonstrated viscosity changes that are mainly due to changing the composition of liquid phase and its viscosity, especially when calculated by FS. The s23-2 slag, which has intermediate viscosity values (between 10 and 100 Pa·s), showed that the overall viscosity increases more dramatically than that above the $T_{\rm liq}$ due to both solid growth and changes in the viscosity of liquid phase. In the low-viscosity s27-1 slag (5–15 Pa·s), the solid content contributed more to the viscosity increase than did the changes in the liquid-phase composition according to the K–F calculations.



Figure 7. Correction of the Kalmanovitch–Frank (K-F) and FactSage (FS) model predictions for s11-1 (a), s27-1 (b), and s23-2 (c) slags.

However, the solid content had less impact on the viscosity increase according to the FS calculations.

The effective viscosity can be calculated as the ratio of the experimental overall viscosity and the viscosity of the residual liquid adjusted, as described above. Figure 8a–c shows the effective viscosity vs volume fraction of the solids; the viscosity of the residual liquid was calculated by the corrected K–F and FS models (open squares and diamonds, respectively) for the three selected slags. Also shown in Figure 8 are predictions by the classical Einstein²⁰ (eq 2) and Roscoe²¹ (eq 3) models:

$$\eta_{\rm eff} = 1 + 2.5\phi \tag{2}$$

$$\eta_{\rm eff} = (1 - 1.35\phi)^{-2.5} \tag{3}$$

In general, the classical model predictions were lower than the experimental values when liquid viscosity was predicted by the K–F model. The Roscoe equation fitted the experimental results perfectly for the s27-1 slag when the FS predictions of the liquid-phase viscosity were used. However, in the latter case, the experimental values obtained for the s11-1 slag appeared to be even lower than the Einstein predictions for very dilute solid concentrations (less than 1 vol %). This indicates that, at least for this slag, the FS model overestimates the viscosity of the residual liquid phase. The classical model predictions were also much lower than the experimental values obtained for the s23-2 slag (Figure 8c).

The effective viscosity values obtained by various studies on heterogeneous slags containing different spinel crystals are compared in Figure 9. A spinel phase can have very different chemical composition, depending on the bulk slag composition. For example, in the present work, the spinel phase is primarily MgAl₂O₄ (true spinel) with a small addition of FeAl₂O₄ (hercynite). Wright et al. added MgAl₂O₄ particles into a liquid CaO-MgO-Al₂O₃-SiO₂ slag²² and Fe₃O₄ (another spinel phase: magnetite) particles into a CaO-FeO slag.²³ Despite their variable composition, the structure of any spinel phase is very similar. Generally, it represents a solid solution of $X^{2+}Z_2^{3+}O_4^{2-}$, where X can be Ca, Mg, Fe²⁺, etc. and Z can be Al, Fe³⁺, Cr³⁺, etc. Crystals of any spinel phase also have the same cuboid shape. The spinel phase obtained in the present work (samples s11-1, s23-2, and s27-1) have a similar size (approximately 5–20 μ m) of crystalline particles, while Wright et al. used different particle sizes from "fine" (100-210 μ m) to "coarse" (440–990 μ m). The solid line in Figure 9 represents a fit of the Krieger-Dougherty equation (eq 4):²⁴

$$\eta_{\rm eff} = \left(1 - \frac{\phi}{\phi_{\rm m}}\right)^{-[\eta]\phi_{\rm m}} \tag{4}$$

into the experimental data (all points except those with a large deviation) with $\phi_{\rm m} = \pi/6$ and $[\eta]$ as an adjustable parameter $([\eta] \approx 6.1)$.

The results obtained for samples of s11-1 and s27-1 and those from Wright et al.²² with "fine" particles demonstrate that the viscosity values reasonably close to the Krieger-Dougherty value fit. However, some spinel-containing slags (e.g., black triangles, black circles, and open diamonds in Figure 9) showed a large deviation from the Krieger-Dougherty trend. For the results by Wright et al.^{22,23} (black triangles and circles), this deviation can be accounted for by the presence of big spinel crystals over 400 μ m, while in the case of s23-2, the deviation could be associated with a different crystallization mechanism, as discussed in the following section. Moreover, the calcium-ferrite slag (closed black circles) initially had a very small viscosity of the liquid phase, which may be a possible reason for the dramatic increase in the effective viscosity as a function of the solid volume fraction. The other results (i.e., s23-2 in the present work and the one with big crystals in the CaO-MgO-Al₂O₃-SiO₂ slag in ref 22) demonstrated a relatively small increase in the effective viscosity when the solid volume fractions reached 0.04 and 0.07, respectively. It appears that the behavior of the crystalbearing slags is therefore more complex than that described by the classical suspension models.

3.5. Crystallization Kinetics of Spinel. It was demonstrated in the previous section that, when the viscosity models with the solids are applied at temperatures below liquidus, the solid content is usually estimated using thermodynamic calculations of slag phase equilibria. These approaches are effective in slag flow modeling except for an operating



Figure 8. Effective viscosity as a function of the volume fraction of solids for s11-1 (a), s27-1 (b), and s23-2 (c) slags. Residual liquid viscosity was estimated by the Kalmanovitch–Frank (K–F) and FactSage (FS) models.



Figure 9. Effective viscosity vs the volume fraction of solids showing the experimental results of this work and of Wright et al.^{22,23}

condition when the resident time of the slag flow inside the entrained flow gasifiers is comparable or longer than the time required for slag crystallization (solid growth). For this operating condition, we need a submodel that can estimate the transient solid growth rate of the slag in order to calculate the apparent viscosity of the subliquidus slag accurately.

Slag phase composition (and therefore, the concentrations of the solids), listed in Table 3, depends on the time for which slags are kept at a certain temperature during viscosity measurements. Figure 6 demonstrates that, even though the concentration of solids for slag s11-1 determined from the slag microstructure is close to that calculated by FS, phase equilibria was not reached in some slag compositions before the slags were quenched. The kinetics of spinel isothermal crystallization strongly depends on slag viscosity,²⁵ and it takes few hours for high-viscosity slags to reach phase equilibria.⁶

We have previously described a method based on viscosity measurements that can predict isothermal solid phase growth, particularly in slags with spinel solids.²⁵ When apparent slag viscosity measurements are conducted at temperatures below $T_{\rm lig}$ and samples are kept at a certain temperature after the temperature has decreased, it is possible to observe a change in viscosity induced by the solid growth. This is especially the case if the kinetics of slag crystallization are relatively slow. If solids do not precipitate quickly, the slag thermodynamic "response" to temperature begins after the slag reaches the desired temperature. From that point, all viscosity changes should be associated only with solid phase growth. For the Newtonian flow demonstrated for slags with spinel crystals in the present study, there should be gradual apparent viscosity growth until crystallization is completed and the slag reaches the phase equilibrium state. A detailed interpretation of the spinel growth kinetics from the slag apparent viscosity changes is presented elsewhere.²⁵

According to Nofar et al.,²⁶ the kinetics of isothermal melt crystallization at different isothermal temperatures can be analyzed using the Kolmogrorov–Johnson–Mehl–Avrami (KJMA) equation²⁷ (eq 5).

$$\emptyset(t) = 1 - \exp(-kt^n) \tag{5}$$

where k is the crystallization kinetic constant for nucleation and growth rate and n is the Avrami exponent reflecting the mechanisms of crystal nucleation and growth. In this study, using our experimental data, the Avrami exponent, n, and the logarithm of the kinetic constant, ln k, were determined by plotting $\ln[-\ln(1 - \varpi(t))]$ vs $\ln(t)$. The results plotted in Figure 10 demonstrate the kinetics of spinel phase growth until the equilibrium state is achieved (for s23-2 at 1275 °C) or nearly achieved (for s11-1 at 1270 °C and s27-1 at 1250 °C). The graphs show that the KJMA equation could not estimate the transient trend of isothermal melt crystallization very well,



0 1000 2000 3000 Time (s)

Figure 10. Transient trend of the increase of melt crystallization at isothermal temperatures of 1270 $^{\circ}$ C for s11-1 (a), 1250 $^{\circ}$ C for s27-1 (b), and 1275 $^{\circ}$ C for s23-2 (c).

especially at the end of the process where crystallization is slowing down. For that reason, we propose another approach, which includes \emptyset_{eq} , the solid fraction at phase equilibrium.

In our approach, the rate of transient isothermal melt crystallization, *R*, is defined as

$$R = \frac{\text{solid fraction growth per second}}{\text{potential maximum solid growth at time } t} = Kt^{N}$$
(6)

where potential maximum solid growth at time t, $\mathscr{O}_{p}(t)$, is defined as

$$\mathscr{Q}_{\rm p}(t) = \mathscr{Q}_{\rm eq} - \mathscr{Q}(t) \tag{7}$$

So, the differential equation of the growth rate can be written as

$$\frac{\mathrm{d}\mathscr{B}_{\mathrm{p}}(t)}{\mathrm{d}t} = -[\mathscr{B}_{\mathrm{p}}(t)]Kt^{N} \tag{8}$$

When one integrates eq 8 within the limits between time t_0 and t, the solid fraction, $\emptyset(t)$, can be calculated using eq 9:

$$\mathscr{O}(t) = \mathscr{O}_{eq} \left[1 - \left(1 - \frac{\mathscr{O}(t_0)}{\mathscr{O}_{eq}} \right) (\exp(-kt^n)) \right]$$
(9)

where $k = \left[\frac{K}{N+1}\right]$, n = N + 1.

When one takes the log from both sides of eq 9, it can be written as

$$\ln\left[-\ln\frac{[\mathscr{Q}_{\rm eq} - \mathscr{Q}(t)]}{[\mathscr{Q}_{\rm eq} - \mathscr{Q}(t_0)]}\right] = \ln(k) + n\ln(t)$$
(10)

Using our experimental data, the exponent, *n*, and the logarithm of the kinetic constant, ln *k*, can be determined by plotting $\ln \left[-\ln \frac{[\emptyset_{eq} - \emptyset(t)]}{[\theta_{eq} - \emptyset(t_0)]} \right]$ vs ln(*t*).

Using eq 10, the transient trend of isothermal melt crystallization for different samples under different isothermal conditions was calculated, and the agreement between the model and experimental data was excellent (see Figure 10). The experimental data for the solid fraction in Figure 10 are calculated from experimental apparent viscosity data using eq 4. Note that eq 10 includes two more parameters: solid fraction at time t = 0 and solid fraction at the equilibrium condition. The model parameters k and n were calculated for all cases, with the results listed in Table 5. As the samples listed

Table 5. Model Parameters to Calculate the TransientGrowth of Isothermal Melt Crystallization

sample	temperature (°C)	ϕ at equilibrium (vol %)	k	n
s11-1	1250	6.15	6.670×10^{-3}	0.658
	1270	5.80	4.468×10^{-3}	0.643
	1290	5.70	1.162×10^{-2}	0.439
s27-1	1250	9.00	2.180×10^{-3}	0.728
	1275	8.80	1.926×10^{-3}	0.711
s23-2	1250	2.63	8.290×10^{-4}	1.160
	1275	2.25	1.443×10^{-3}	1.067
	1300	0.46	5.422×10^{-2}	0.643

in the table were processed by step cooling, the initial solid fractions at the beginning of crystallization at the highest temperatures are 0 vol %. The initial solid fractions at lower temperatures are the same as ϕ at equilibrium at the previous temperature of isothermal crystallization.

The theory of diffusion-controlled growth of crystallizing species has been reviewed by Macfarlane,²⁸ who proposed various possible growth morphology and nucleation conditions identified and classified by the value of the Avrami exponent, *n*. According to Macfarlane,²⁸ the Avrami exponents of s11-1 and s27-1 are closer to 0.5 (especially the *n* values of s11-1), which implies that the crystallization mechanism of s11-1 could be taken as the diffusion-controlled surface nucleation with one-dimensional growth. In contrast, the *n* value of s23-2 is close to 0.5 only at the beginning of the crystallization (at 1300 °C); at

Article

lower temperatures, it is close to 1. This suggests that the crystallization mechanism of s23-2 is likely to be diffusioncontrolled growth with instantaneous nucleation.²⁹ The changes in the Avrami exponent, *n*, under different crystallization temperatures plotted in Figure 11 show that *n* values seem constant within a certain temperature range (i.e., <1270 °C) and decrease significantly at higher temperatures.



Figure 11. Trend of the Avrami exponent, *n*, at different temperatures for selected coal slags.

4. CONCLUSION

In this study, we have investigated viscosity, phase compositions, and solid-phase growth in brown coal slags from the spinel primary phase field at temperatures corresponding to the operating temperature range of entrained-flow gasifiers. Our key findings are summarized as follows:

- All brown coal ashes investigated have a slag viscosity range sufficient for tapping in entrained-flow gasifiers at a temperature range of 1400–1550 °C.
- Most slag compositions are in the spinel primary field: even if parent coal slag is in the mullite primary phase field, sodium enrichment moves the slag composition to the spinel primary phase field.
- For all investigated slag compositions, sodium enrichment decreases slag viscosity, slag liquidus temperature, and solid content below liquidus.
- At temperatures below T_{liq} , slag viscosity still demonstrates Newtonian flow behavior with a solid content of up to 9 vol %.
- The kinetics of spinel isothermal crystallization strongly depend on slag viscosity, and solid-phase growth may take up to a few hours before it reaches phase equilibria.

The experimental data obtained in this study was applied to develop slag viscosity and solid-phase growth models. Our main findings are

- The Kalmanovitch–Frank and FactSage models predict the viscosity of the investigated slags relatively well. These models were adapted to describe the viscosity of fully liquid slag in the compositional range used in this study.
- Viscosity data of three slags with spinel crystals were used to evaluate models of the effective viscosity of slags with solids. Two slag compositions demonstrate a trend reasonably close to the Krieger–Dougherty fit; however, viscosity behavior of crystal-bearing slags is more

complex than that described by the classical effective viscosity models.

- A kinetic model of spinel phase growth was developed by modifying the Kolmogrorov–Johnson–Mehl–Avrami equation to fit the experimental data obtained during isothermal slag crystallization at the viscosity measurements.
- The Avrami exponent, *n*, representing the mechanisms of nucleation and crystal growth, and the effective overall reaction rate, *k*, were determined for slags with spinel crystals.

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Notes

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