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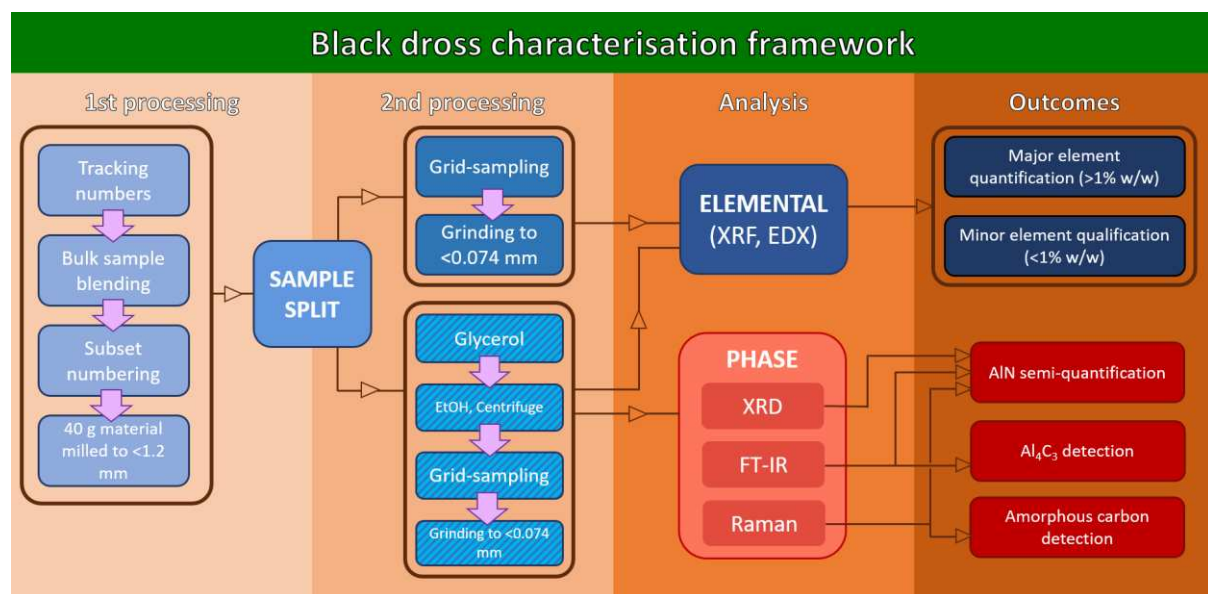
Characterisation of aluminium black dross before and after stepwise salt-phase dissolution in non-aqueous solvents

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Graphical abstract



Highlights

- The glycerol pre-treatment method is an effective way to assist in determining minor reactive phases.
- The problematic mineral phases associated with AlN could be easily identified after pre-treatment.
- The existence of amorphous or turbostratic graphitic carbon in black dross has been confirmed.
- The FT-IR allowed the successful identification of Al₄C₃ presence in industrial samples of black dross.

36 Abstract: Aqueous leaching to recover salts from black dross is accompanied by hazardous
37 gas generation. The gas-generating phases vary significantly across differently sourced black
38 dross. The challenge for industry is how to accurately qualify and quantify the problematic
39 components of black dross, especially minor reactive phases. This paper employed XRF,
40 EDX, XRD, Raman and FTIR to analyse two industrial black dross samples from various
41 sources. A novel pre-treatment method before characterisation was devised using water-free
42 glycerol and anhydrous ethanol to remove the major salt components, without reacting the
43 gas-generating phases. The results show that around 80% of the salts existent in the black
44 dross had been removed successfully through pre-treatment. This method facilitated the
45 determination of minor reactive phases characterised by XRD, XRF and EDX, and had little
46 effect on the characterisation by Raman and FTIR spectroscopy. The ammonia-generating
47 nitride phase was detected by XRD, Raman and FTIR. The FTIR, moreover, allowed the
48 successful identification of carbide. Best practice guidelines for the industrial analysis of
49 black dross has been proposed. The guidelines would provide industry with evidence to
50 include or adjust gas treatment methods and operational parameters when dealing with
51 compositional variability in industrially-sourced black dross.

52
53 Keywords: Aluminium black dross, characterisation, hazardous waste, salts dissolution,
54 aluminium nitride

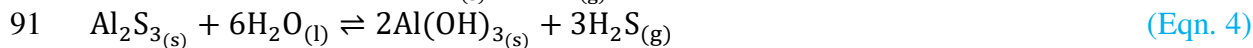
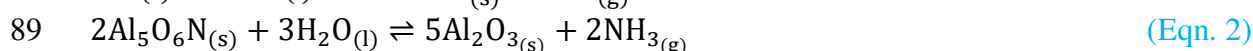
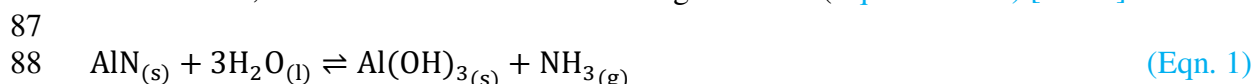
55 56 1. Introduction

57
58 Due to its unique physical and chemical properties, aluminium (Al) has been widely used in
59 the automobile, aerospace, architectural construction, and marine industries, as well as having
60 many domestic uses [1, 2]. At present, Al is mainly produced via two different routes [3]:
61 primary Al extracted from bauxite ore and secondary Al recycled from scrap and white dross
62 (produced during primary Al production). In the past three decades, approximately 80 million
63 tons of Al has been produced and more than 26 million tons of scrap recycled [4].

64
65 In the secondary Al industry, the Al scrap and white dross are re-melted in a furnace with the
66 addition of a large amount of salt flux. The salt flux can effectively help the agglomeration
67 and separation of the molten Al from the solid oxide fraction and protect the metallic Al
68 against oxidation [5]. During the melting process, non-metallic components are absorbed in
69 the liquid flux, forming a by-product referred to as black dross. The black dross is removed
70 by skimming off the top layer of the liquid melt. Depending on the scrap mixture feed,
71 approximately 200-500 kg of black dross is produced per ton of Al [6-8]. In general, black
72 dross contains a large amount of the salt-flux mixture (e.g., NaCl, KCl and fluorides), metal
73 oxide (e.g., Al_2O_3), a small amount of fine metallic Al particles, and some minor
74 contaminants (e.g., Al_4C_3 and AlN) [9].

75
76 Black dross has been classified as a hazardous and toxic waste by the EU since 2000 [10] and
77 exposure is considered detrimental to both the environment and human health. Specifically,
78 black dross is considered hazardous with respect to carcinogenicity and skin
79 corrosion/irritation. The non-metallic product (NMP) component of black dross is also a
80 sensitizer and irritant through prolonged or repeated skin or mucous membrane contact [4].
81 The dust generated from handling black dross is a significant hazard with respect to ingestion
82 and inhalation. In addition, active contaminants in black dross are very sensitive to moisture
83 and react to produce harmful, explosive, poisonous, and unpleasant odorous gases [11, 12].
84 Potential contaminants AlN, Al_4C_3 , AlP, Al_2S_3 , and Al_5O_6N present in black dross can

85 hydrolyse in contact with water producing gaseous ammonia, phosphine, hydrogen sulphide,
86 and methane, in accordance with the following reactions (Equations 1-5) [13-15].



93
94 This reactivity means that disposal of this waste material must be strictly controlled and to
95 avoid/minimise environmental pollution, only controlled landfills can be used for the disposal
96 of black dross [16]. Previously, around 95% of the industrially produced black dross was
97 landfilled each year [8]. However, the residual 5% has been steadily accumulating, due to
98 continuing Al production. This current waste stream, including legacy material, needs to be
99 treated urgently, to avoid accidental environmental releases. At present, changing public
100 consciousness and solicitousness regarding the state of the environment is forcing legislators
101 to pass more rigid regulations on pollution. This changing landscape of environmental
102 regulation is also accompanied by a subsequent increase in disposal costs [17]. Consequently
103 the development of a sustainable economic and environmentally-friendly process that can
104 recycle black dross into valuable products is highly sought after by industry [18].

105
106 To permit the efficient recovery of the salt flux content of black dross, solubility dictates that
107 an aqueous process is the only sensible option for industrial processing. However, Scharf *et al.*
108 investigated aqueous leaching of black dross, finding that on average, 57 cm³ of gas was
109 produced per gram of black dross treated [19]. It is imperative that the potential
110 environmental risks of gas emission from dross treatment need to be considered. It would
111 suggest that extensive gas removal would be a pre-requisite for any industrial scale leaching
112 process [20, 21]. The combustible toxic gases produced by aqueous leaching of black dross
113 could be abated in a number of ways: Hydrogen sulphide generated during the process could
114 be oxidised in the dissolution process by addition of hydrogen peroxide [22]. Use of alkaline
115 leaching conditions would lead to the production of ammonia which can be removed by
116 H₂SO₄ / water scrubbers [3]. Phosphine gas produced could potentially be oxidized to
117 produce phosphate fertilizer by a catalytic reaction or absorbed onto activated carbon [3].

118
119 Because of the different starting raw materials and metallurgical processes used in secondary
120 Al production, the chemical, mineralogical, and elemental composition of the black dross can
121 vary significantly from source to source [23]. This wide variability in black dross matrix and
122 the potentially different hazardous gases generated would necessitate subsequent adjustments
123 to both gas treatment methods and operational parameters every time an industrial plant dealt
124 with a different type of black dross. To inform changes to industrial processing conditions, it
125 is paramount that the reactive components in each black dross feed be identified. An
126 analytical process that allows the quantitative and qualitative identification of these reactive
127 components in black dross is vital to supporting the development of an economical,
128 sustainable and environmentally friendly process of black dross treatment, which does not
129 rely solely on an expensive controlled landfill option. In previous work, researchers
130 employed XRF and XRD for the chemical and mineralogical analysis which cannot detect all
131 of the harmful components in samples. AlN can only be detected when the content is high
132 (normally over 3%). [4, 24, 25]. So far, there is no literature report that Al₄C₃ in black dross
133 has been identified by XRD. In this paper, samples from two different industrial sources were

134 investigated by using various solid-state microstructure characterization techniques. Besides
135 XRF and XRD, another three techniques EDX, FTIR and Raman spectroscopy were
136 introduced, to investigate the mineralogy in detail trying to identify more reactive mineral
137 phases. This is the first use of FTIR and Raman in the literature to characterise black dress.
138

139 In addition, compared to the large concentration of salts in black dress, the minor toxic gas
140 generating phases are difficult to determine using solid state characterisation methods [3]. We
141 found that the salt phases (such as NaCl, KCl) showed significant solubility in glycerol (the
142 salt phases are about 0.25 times as soluble in glycerol as they are in water) without reacting
143 with the gas evolving species [26]. In this paper, we have developed a novel pre-treatment
144 method to separate the salts from black dress by dissolving them in dry glycerol, without
145 changing the original status of these minor gas generating phases. Since dry glycerol is very
146 viscous and its boiling point is 290 °C [27], it is difficult to remove residual salt-containing
147 glycerol absorbed to the surface of the black dress particles. To solve this issue, anhydrous
148 ethanol was used to wash away residual salt-bearing glycerol from the remaining black dress
149 particles. In this way, the treatment works as a pre-concentration method, where the
150 concentration of non-salt phases in as-received black dress increases. The minor reactive
151 phases can therefore be more readily identified than before pre-treatment. To the best of our
152 knowledge, this pre-treatment of black dress before characterisation has not been reported
153 previously.
154

155 Besides, our study, for the first time, has summarised the optimum steps and methods for the
156 characterization of black dress as soon as sample arrives at the plant, accordingly establishing
157 a practical guideline for black dress analysis prior to processing. The establishment of
158 analytical best practice would assist industry in predetermining on plant gas abatement
159 processes and operational parameters. This work is part of an ongoing project to help inform
160 industry with respect to developing an economical and sustainable black dress salt recycling
161 process.
162

163 2. Experimental

164 2.1. Materials

165
166 Samples with an average particle size of less than 1.2 mm from two different industrial
167 sources were provided by Altek and designated as A₀ and B₀ in this study. Additionally, the
168 two samples after salt-dissolution treatment were named A₁ and B₁, respectively. All
169 chemical reagents were supplied by Sigma Aldrich at analytical grade or higher, and were
170 used as received. The anhydrous solvents after opening were stored over 5 Å molecular
171 sieves to remove water.
172

173 2.2. Salts dissolving tests

174
175 In the dissolution tests, 20 g of black dress sample (A₀ or B₀) was added to 400 mL of
176 anhydrous glycerol (40 min contact, 175 rpm agitation, 25 °C). The remaining residual solid
177 was separated by centrifugation (15 min at 4000 rpm). The residual solid (A₁ or B₁) was
178 washed and centrifuged (15 min at 4000 rpm) 3 times with anhydrous ethanol. The solid was
179 then dried in an air-flow oven at 60°C for 24 hours.
180

181
182 A comparison sample was prepared by dissolving 20 g of black dress samples in 400 mL
183 water for 10 minutes (through initial experiments, we observed that, with aqueous treatment,

184 increasing the contact time further did not result in better leaching) with the same agitation
185 and temperature conditions. The residue was then filtered and dried in an air-flow oven at
186 60°C for 24 hours.

187

188 2.3. Sample preparation and characterisation tests

189

190 Before microstructural characterisation by XRF, EDX, XRD and Raman, all samples were
191 ground to fine particles (-0.074mm) using a pestle and mortar. 1 g sample powder was
192 pressed into a tablet (with a diameter of 1.2 cm) using a Powder Tablet Press Machine
193 (Specac Manual Hydraulic Press).

194

195 A XRF spectrometer (PANalytical, Zetium model) and a FEG-SEM (FEI NOVA450),
196 equipped with an EDX detector, were employed for elemental quantification. XRF has been
197 done twice and the results were averaged for each sample. The EDX mapping scan has been
198 done twice for each area data collection. XRD data were collected using a Bruker D2
199 PHASER instrument (Cu K- α radiation, 0.15418 nm). The tube voltage and current, step
200 time, increment and scanning range were 30 kV and 10 mA, 0.4 s, 0.02°, 10°-90°
201 respectively. The powder diffraction file (PDF) patterns database from the International
202 Centre for Diffraction Data (ICDD) was used for identification and semi-quantification.

203 Raman spectroscopic measurements were carried out using an inVia Raman Microscope,
204 with a laser (514.5 nm, ~2.5 mW) excitation source. The Charge Coupled Device (CCD)
205 exposure time was 20 s and every sample was scanned 2 times. Raman spectral data were
206 generated from 50 cm⁻¹ to 4000 cm⁻¹.

207

208 FTIR spectroscopy was carried out using a Perkin Elmer Lambda 900 UV/Vis FTIR
209 Spectrophotometer. Samples were prepared for analysis by grinding a known mass of solid
210 with anhydrous Potassium bromide. The sample powder was then pressed at 1000 tons for 1
211 min and then pressed at 10000 tons for 1 min to produce a pellet for analysis. The
212 wavenumber ranges analysed were from 600 cm⁻¹ to 4500 cm⁻¹.

213

214 3. Results

215

216 3.1. Salt dissolution sample preparation

217

218 Water-washing was used to compare the effectiveness of salt-dissolution by glycerol. Table 1
219 compares the weights of samples obtained before and after sample-washing with dry glycerol
220 and water. All dissolution experiments were conducted at least two times. Errors listed in
221 Table 1 were generated by the standard deviation of duplicate measurements. As shown in
222 Table 1, sample weights obtained after salt-dissolution in glycerol were 11.39g and 13.87g
223 for samples A and B, representing 43.05% and 30.66% weight loss through the pre-treatment
224 process. The corresponding weights of samples A and B, after water-washing were 10.10g
225 and 7.30g respectively, representing 49.50% and 36.50% weight loss for each sample. It can
226 be clearly seen that both samples contained a high concentration of salts and glycerol showed
227 good dissolving ability compared to salts dissolving in water. The large discrepancy in mass-
228 retention between the two samples illustrates the variable composition of black dross,
229 depending on its source.

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Table 1. Comparison of sample weights obtained before and after salt-dissolution in glycerol and water (175 rpm agitation, 25 °C)

Sample		Sample A		Sample B	
		A ₀	A ₁	B ₀	B ₁
		before salt-dissolution	after salt-dissolution	before salt-dissolution	after salt-dissolution
Glycerol washing (40 min contact)	Mass (g)	20.00±0.01	11.39±0.01	20.01±0.01	13.87±0.01
	Δg (g)		8.61±0.02		6.14±0.02
	Δg (%)		43.05±2.00		30.66±2.00
Water washing (10 min contact)	Mass (g)	20.00±0.01	10.10±0.01	20.00±0.01	12.70±0.01
	Δg (g)		9.90±0.02		7.30±0.02
	Δg (%)		49.50±2.00		36.50±2.00

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3.2. XRF analysis

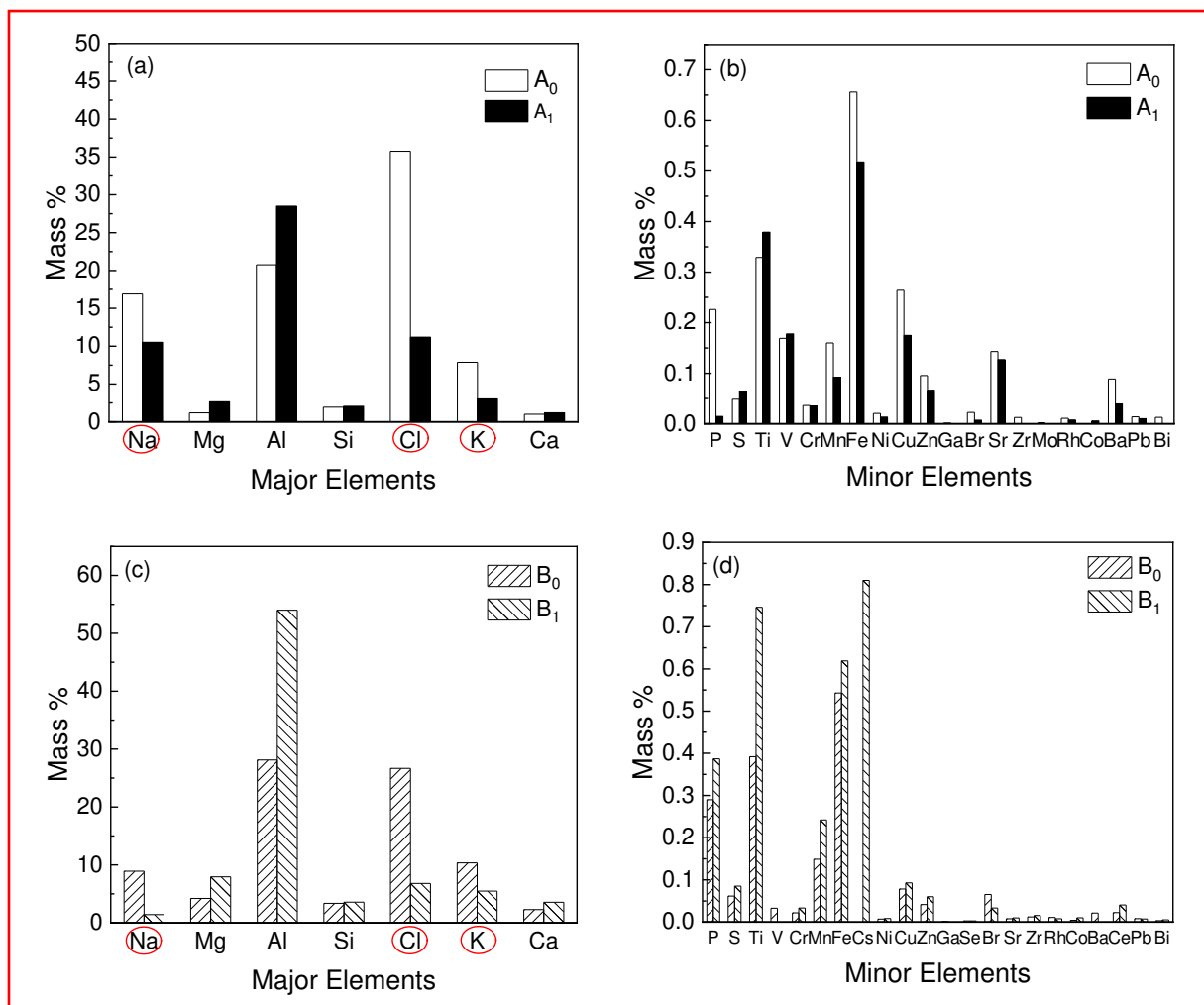
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The chemical compositions of the two sourced samples, before and after pre-treatment, were identified using XRF (Fig. 1), and the specific values are listed in [Table S1 in the supplemental materials](#). Overall, all samples had complex chemical constituents, with 27 and 29 elements detected in sample A and B, respectively. Specifically, 26 elements were found in A₀, 23 in A₁, 28 in B₀ and 26 in B₁. The content of Na, Mg, Al, Si, Cl, K and Ca were all over 1% by weight (Fig. 1-(a) and (c)). These elements were treated as major elements in black dross samples. Comparatively, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Se, Br, Sr, Zr, Mo, Rh, Cs, Ba, Ce, Pb, Bi were minor constituents (Fig 1-(b) and (d)). The two different industrially sourced samples A and B all contained the same types of major elements. However, some of the minor elements were not included in both samples. For example, sample A did not contain Se, Cs and Ce, while Mo did not exist in sample B.

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Fig. 1-(a) and (c) obviously show that after pre-treatment, the salt content Na, K and Cl has been largely decreased (elements are circled in red). In contrast, due to the dissolution of salts from the original samples, the amount of other major elements, (such as Mg, Al, Si, Ca) relatively increased substantially. Obviously, pre-treatment facilitates the observation of these major elements. However, as shown in Fig. 1-(b) and (d), the increasing trends for minor elements after pre-treatment of dissolving salt-phases were not obvious. The reason for this was the minor element amounts after pre-treatments were still too low to be easily detected by XRF due to its resolution.

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Fig. 1. Chemical analysis of aluminium black dross from two different sources before (A_0 , B_0) and after (A_1 , B_1) salt-phases dissolution in glycerol and ethanol by XRF-(a) and (c) Elements with weight content over 1%; (b) and (d) Elements with weight content below 1%

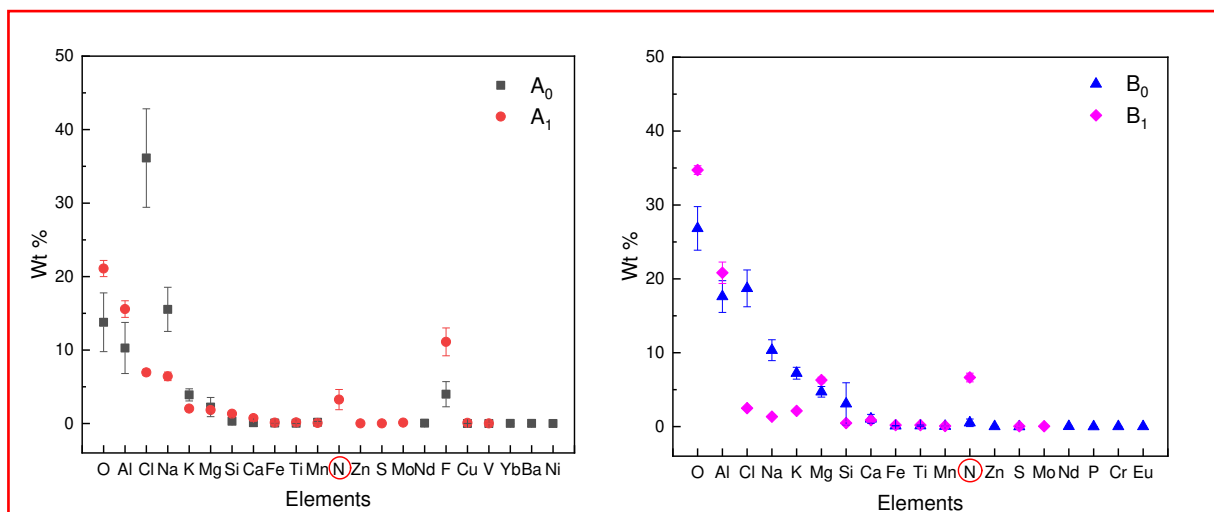
3.2. EDX elemental quantification

268 The chemical compositions of two samples before and after pre-treatment were investigated
269 by EDX mapping from various areas of the samples. Each sample was scanned at least 5
270 different areas, over its whole surface area. The average elemental quantification is shown in
271 Fig.2. It is seen that elements O, Al, Cl, N, Na, K, Mg, Si, Ca, Fe, Ti, Mn, Zn, S, Mo, and Nd
272 were detected in both samples. F, Cu, V, Yb, Ba, and Ni were discovered in sample A, while
273 P, Cr and Eu were only observed in sample B. More specifically, there were 18 elements in
274 A_0 , 18 elements in A_1 , 18 in B_0 , and 14 in B_1 with different minor elements. Compared to
275 XRF results, N, O, F, P and Eu were detected by EDX only. It is obvious that both samples
276 from various sources contained a large number of elements, and showed species variability in
277 the minor contaminant or alloying elements.

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The change in concentrations of elements, shown in EDX analysis, before and after salt-dissolution, was similar to the XRF results. It is clear that the concentrations of elements Cl, Na, K, which majorly contributed to salt phases, were decreased in both samples after pre-treatment. It is noticeable that the problematic element N, which contributes to the formation of nitrides was detected in sample A_1 (circled in red in Fig. 2) after salt-dissolution, yet was not found in sample A_0 . Also, after multiple scans, the detection frequency of element N was

285 higher in the sample B₁ after salt-dissolution. The specific data obtained from multiple scans
 286 can be found in Figure S1 in the supplemental materials.
 287



288
 289 Fig. 2. Chemical analysis of aluminium black dross from two different sources before (A₀,
 290 B₀) and after (A₁, B₁) salt-phases dissolution in glycerol by EDX
 291

292 3.3. XRD analysis

293
 294 The XRD patterns before and after salt-dissolution in glycerol are shown in Fig. 3.
 295 Subsequent to salt-dissolution, the intensity of a number of inorganic salt peaks for both
 296 samples was significantly reduced. In contrast, characteristic peaks of other phases have been
 297 largely magnified and much more obvious. Though some published work has reported that
 298 AlN is a major phase in black dross[4], the amount was usually too low to be detected
 299 compared to the huge amount of other salts present. From Fig. 3, it can be seen that for
 300 sample A₀, AlN was not detected (no peaks observed at 2theta values of 33.226, 36.056,
 301 37.943, 49.838, 59.367, 66.077). However, after salt-dissolution, it could be detected and
 302 analysed easily (sample A₁). From the XRD results of sample B₀ and B₁, the characteristic
 303 peaks of AlN were magnified in B₁ compared to the sample B₀. The values of AlN, semi-
 304 quantified by XRD are listed in Table. 2. The pre-treatment method enabled XRD to detect
 305 those minor and problematic phases existing in residual black dross more easily than in
 306 original samples. This result was highly consistent with the results of N content in the various
 307 samples detected by EDX (Fig. 2).
 308

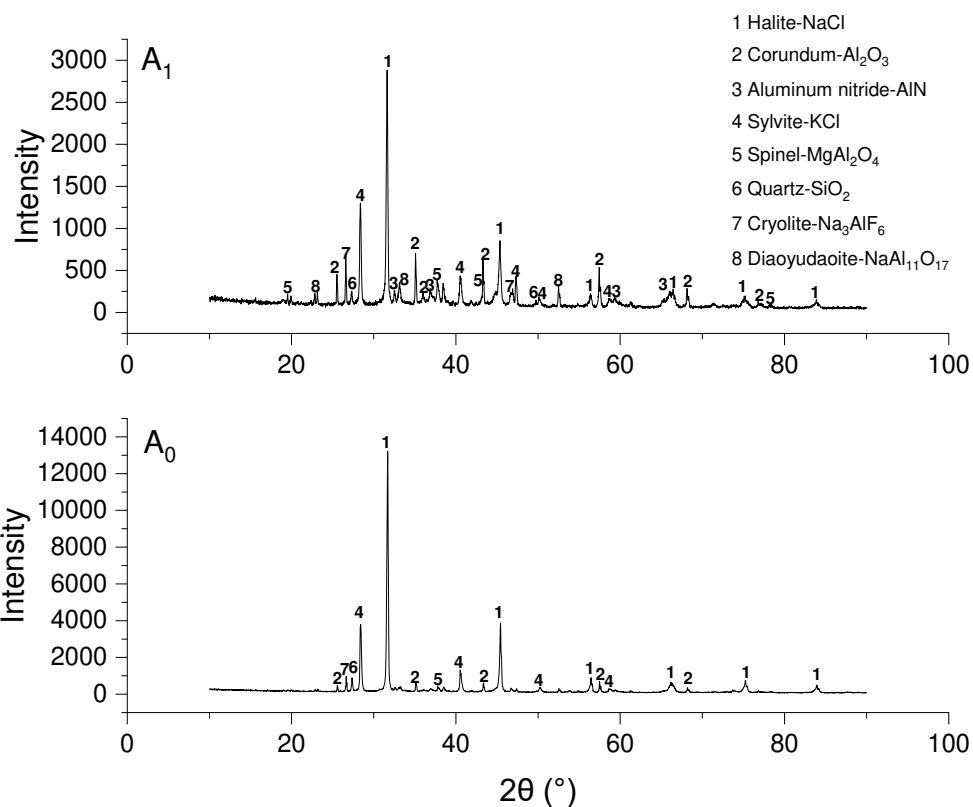
309 Table 2 The content of AlN in the samples from two sources before (A₀, B₀) and after pre-
 310 treatment (A₁, B₁)

	A ₀	A ₁	B ₀	B ₁
AlN content (%)	ND*	3	4	9

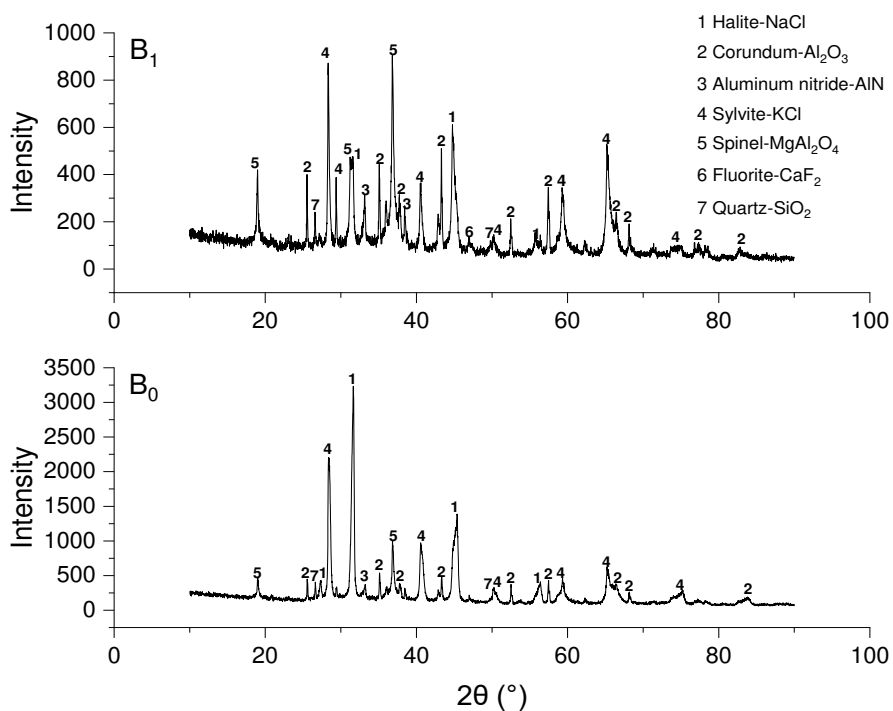
311 * not detectable.

312
 313 Furthermore, halite (NaCl), corundum (Al₂O₃), aluminium nitride (AlN), sylvite (KCl), spinel
 314 (MgAl₂O₄), and quartz (SiO₂) could be identified in both samples A and B. cryolite
 315 (Na₃AlF₆) was found in A₀ and A₁, while Fluorite (CaF₂) was observed in B₀ and B₁. An
 316 extra phase Diaoyudaoite (NaAl₁₁O₁₇) could only be detected in sample A₁. However, the
 317 XRD analysis results did not contain all the elements detected by XRF and EDX results. The
 318 reason for this is that the concentrations of other phases containing those elements were
 319 below the XRD detection limit.

320



321



322 Fig. 3. Mineralogical phases of aluminium black dross from two different sources before (A₀,
 323 B₀) and after (A₁, B₁) salt-phase dissolution in anhydrous glycerol and ethanol
 324
 325

326 3.4. Raman spectra
 327

328 Many mineral-phases contained in black dress are Raman active. It should be noted that the
 329 locations of the peaks were not the same for each curve. Because for heterogeneous samples,
 330 the species abundance in the area of the sample illuminated by the laser spot could not
 331 represent the entire sample, characteristic spectra from some minor mineral phases could only
 332 be identified in some of the scans. Therefore, at least 10 Raman spectra have been done for
 333 an accurate representation of bulk samples. Fig. 4 shows representative Raman spectra for
 334 each sample before (A_0 , B_0) and after (A_1 , B_1) salt-phases dissolution. The Second Derivative
 335 method was used to correct the baselines, using OriginPro software.

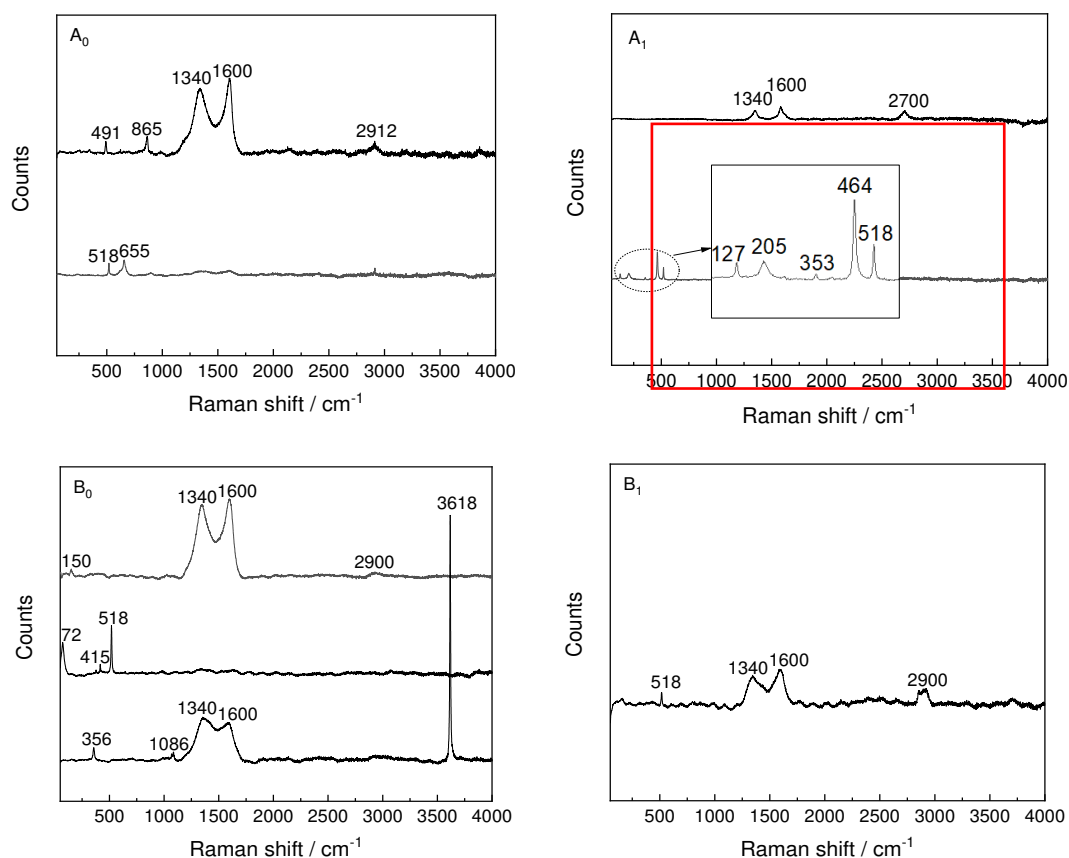
336

337 Based on the Raman spectrum of AlN reported previously [28], the dominant Raman
 338 scattering peak was located at $\sim 658 \text{ cm}^{-1}$. It could therefore be ascertained that AlN was
 339 contained in sample A_0 (Fig. 4). In addition, the huge peaks around 1340
 340 cm^{-1} and 1600 cm^{-1} that were observed in all of the samples, corresponding to the D and G
 341 band regions of carbon, indicated the existence of amorphous or turbostratic graphitic carbon
 342 in the samples [29].

343

344 After salt-dissolution, no new characteristic phase peaks were observed compared to the
 345 species detected before pre-treatment.

346



347

348

349 Fig. 4. Raman analysis of aluminium black dress from two different sources before (A_0 , B_0)
 350 and after (A_1 , B_1) salt-phases dissolution in glycerol and ethanol. Multiple spectral lines in
 351 the same graph represent different analysis points from the same sample.

352

353 3.5. FTIR spectra

354

355 Fig. 5 illustrates the FTIR spectra of the two different samples before (A₀, B₀) and after (A₁,
356 B₁) salt-dissolution. It can be observed that the spectra of samples before and after salt-
357 dissolution are similar for the two sourced samples. Thus, the pre-treatment has little effect
358 on FTIR characterisation.

359
360 According to the spectral repository “SpectraBase” [30], aluminium carbide characteristic
361 peaks would be expected at around 700 and 640 cm⁻¹, which matched perfectly with the FTIR
362 spectra of sample A, indicating the existence of Al₄C₃. This is the first direct identification of
363 the existence of aluminium carbide in black dross, using FTIR spectroscopy. Previous
364 identification methods[31] were inferred indirectly from carbon content assays. It is clear that
365 this previous method can only estimate the existence of Al₄C₃ in black dross, which is
366 inaccurate. The reason for this is evidenced in our study by the Raman spectra, showing
367 obvious characteristic peaks for amorphous or turbostratic graphitic carbon in sample A.
368 Also, as shown in Raman data, sample B still contained carbon. Yet, the FTIR spectra did not
369 show obvious characteristic peaks of Al₄C₃, which indicated that the Al₄C₃ content in sample
370 B was much lower than sample A.

371
372 It is reported that AlN has a dominant characteristic FTIR peak range from 600-1000 cm⁻¹
373 [32]. As shown in Fig. 5, the AlN phase could be confirmed again in sample B by FTIR.
374

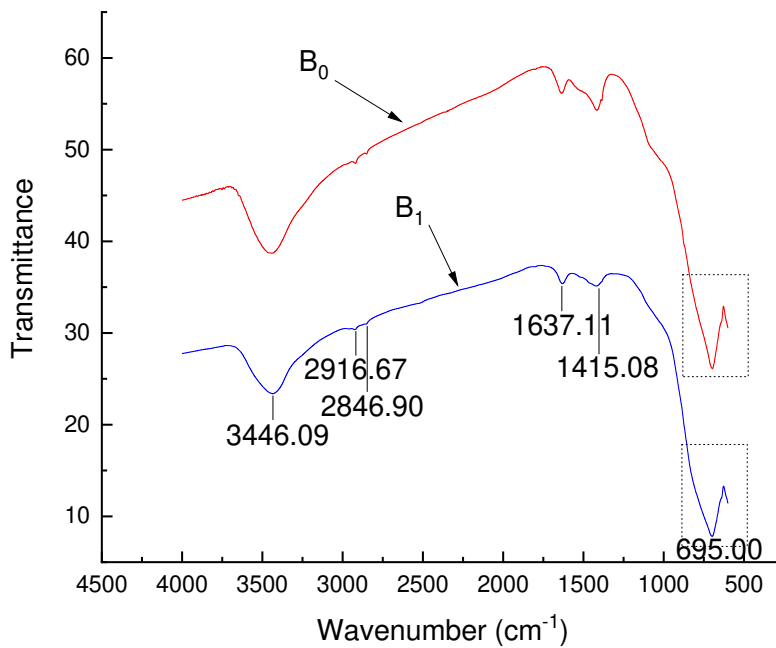
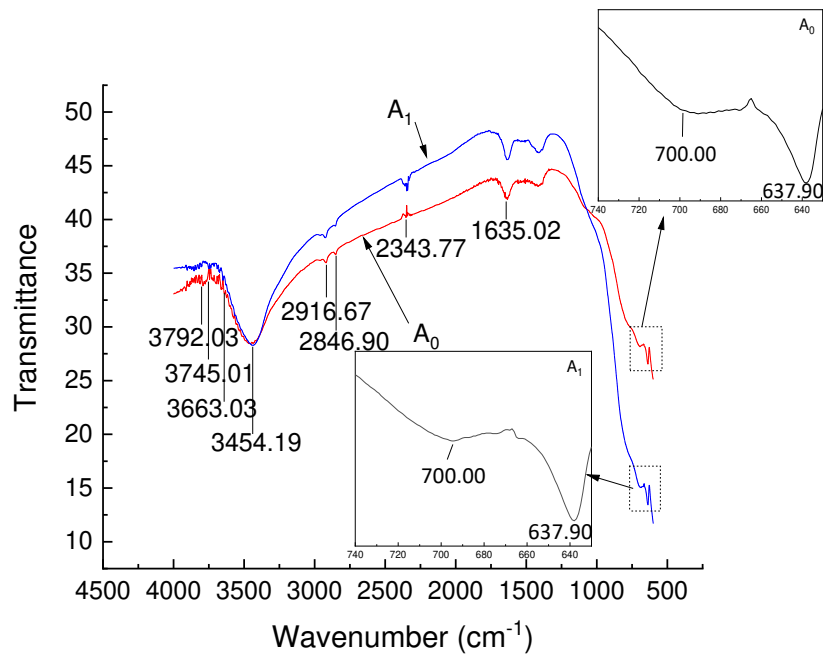


Fig. 5. FTIR analysis of aluminium black dross from two different sources before (A_0 , B_0) and after (A_1 , B_1) salt-dissolution in glycerol and ethanol

4. Discussion

4.1 Improving the industrial characterisation of black dross

A best practice guideline for industrial analysis of black dross is given in Fig. 6. The samples were blended, labelled and collected upon arrival at the processing plant. Each sample was divided into two parts for characterisation preparation: one was directly subjected to

387 preparation, and the other one was processed with further pre-treatment. After that, various
 388 characterisation methods were used for analysis.

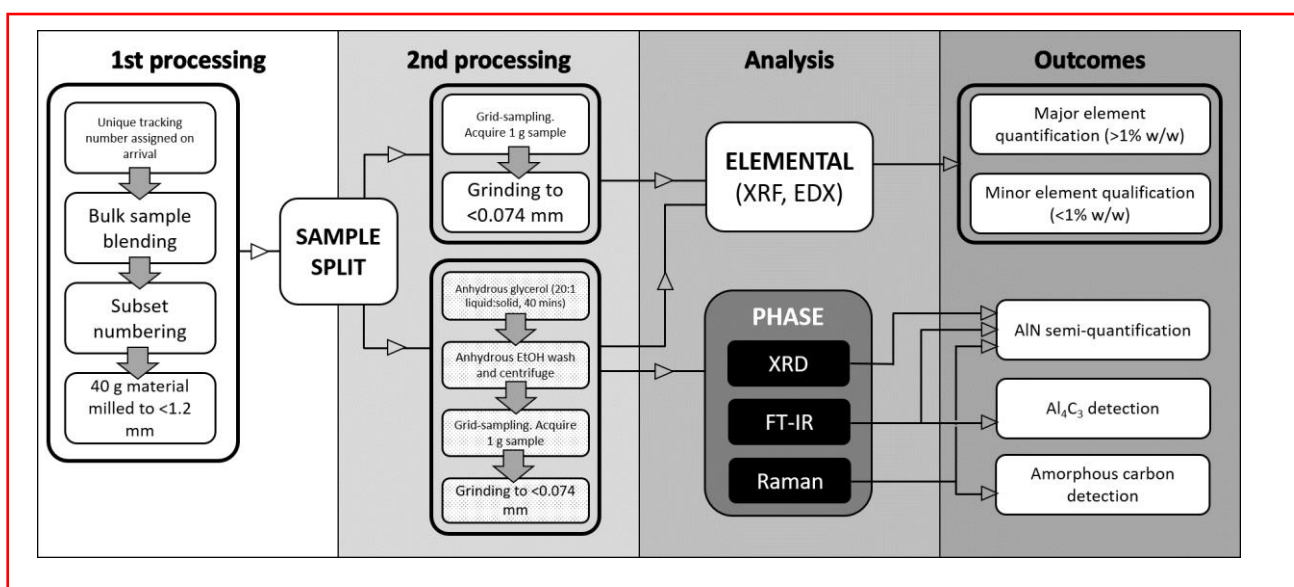
389
 390 In general, it is widely reported that black dross usually contains 40-55% salt-flux mixture
 391 [8]. From our proposed salt-dissolution sample preparation methodology, an observable
 392 weight loss of 43.05% and 30.66% from sample A and B respectively was observed. This
 393 infers that a single sample treatment removes approximately 80% of the salt present in the
 394 black dross sample. This subsequent treatment of glycerol dissolution and ethanol washing
 395 leads to a pre-concentration of non-salt phases by approximately 1.6 and 1.8 times in sample
 396 A and B. This means that more minor phases within the original black dross sample below
 397 the detection limit of different characterisation techniques can exceed the detection limit after
 398 this pre-treatment process. In the future, the salt could potentially be recovered from the
 399 glycerol by solvent evaporation or crystallization, by tuning solvent polarity, but this is
 400 currently beyond the scope of this paper, which is focused upon problematic species
 401 identification. Thus, the salt glycerol phase was not studied further.

402
 403 In this study, the elemental distribution in two sourced samples was characterised by XRF
 404 and EDX. A side-by-side comparison of the elements detected by these two techniques is
 405 shown in Table S2. Obviously, the main difference of elements distributed in various sources
 406 was the existence of different minor alloying elements. Of these, some were detectable only
 407 by XRF (Co, Ga, Br, Sr, Zr, Rh, Cs, Ce, Pb, Bi) and some only by EDX (Nd, Yb, Ba Eu).
 408 The instrument favoured by a particular plant would probably be dictated by economics and
 409 by the level of interest and feasibility in recovering and reprocessing elements of potential
 410 value.

411
 412 Based on phase analysis results, pre-treatment by dissolving salt phases in glycerol and
 413 ethanol was beneficial, in allowing for characterisation of reactive phases present in black
 414 dross. XRD data could reflect more accurately AlN figures, while FTIR allowed the detection
 415 of Al₄C₃. In addition, amorphous carbon could be identified by Raman.

416
 417 It can be seen that following the guidelines in Fig.6, more detailed components of black dross
 418 could be identified clearly to inform plant treatment processes.

419



420

421

422

423

Fig. 6 A guideline of black dross analysis in the industry

424 4.2 The effect of feed variability on the characterisation and salt recycling process

425

426 In this study, more than 8 phases and nearly 30 elements have been identified in black dross.
427 The various **constituents** can be attributed to a great variety of alloying elements **existing** in
428 Al scraps and the differences in operating practices when various Al alloys **are** produced [3,
429 23, 33]. **Specifically**, NaCl, KCl and CaF₂ originated from the molten salt flux, which is
430 commonly used during the melting process. The corundum came from the reaction of the
431 atmospheric oxygen with molten metallic aluminium at high temperatures. MgAl₂O₄ was the
432 result of oxidation of Mg present in the Al scrap as an alloying element during melting. As
433 reported [4], black dross may also contain CaCO₃ which was not detected in our study. This
434 could be attributed to the partial carbonization of portlandite Ca(OH)₂, previously formed
435 during hydration of CaO.

436

437 Not all the contamination phases, such as nitrides, carbides, phosphide **and** sulphide, could be
438 readily detected. AlN can be easily formed, due to the negative Gibbs energy below 283.6 K
439 of the reaction between molten Al and atmospheric nitrogen, occurring after the removal of
440 black dross from the melting furnace [34-36]. Al₄C₃ is formed when molten Al **reacts** with
441 dispersed carbon particles. These **are** introduced from scraps such as paints and plastic
442 coatings on Al cans **and** absorbed by the salt slag during the melting process [3, 21].
443 Aluminium phosphide and sulphide, which have not been found in our study, could be
444 formed through the reaction of Al with phosphates and sulphates in the feed [3, 37].

445

446 Black dross is not only complicated, but also diverse in **nature, according to site of origin**. It
447 is reported that the variability of mineral composition **exists** not only across plants, but within
448 samples from the same plant as well [7]. Here we only focus on the range of **contaminating**
449 phases. Huang [7] investigated 39 samples from 10 different plants, which showed that the
450 average content of AlN contained in the sample was 4.6%, (range: 0-10%). **Other work** [9,
451 20, 34, 37-42] **has** reported that salt cake from secondary Al processing can contain 0-30%
452 Al. Xiao **et al.**[21] has reported that typical salt slag contains: 1% AlN, 7-8% Al₄C₃, and
453 about 0.1% AIP.

454

455 For **the salt-recycling process**, the **feed** variability determines the different methods and
456 operational parameters **for toxic contaminant treatment** during processing. Some sources of
457 black dross contain a high amount of nitride, while **others** contain carbides. This requires
458 industry to add abatement methods for the generated gases, since the possible generated gases
459 (**Equations 1-5**) ammonia, phosphine and hydrogen disulfide are highly toxic. Methane is
460 flammable and a more potent greenhouse gas than CO₂. As **our results show** (Figs.1-5), the
461 problematic phases were AlN in both samples, and Al₄C₃ in sample A. Although AlN was not
462 detected in sample A₀ before pre-treatment, 3% AlN was detected after **salt-dissolution** using
463 **the** pre-treatment process. For sample B, 4% and 10% AlN were determined before and after
464 pre-treatment. **Considering possible** treatment methods, H₂SO₄ / water scrubbers should be
465 added to treat ammonia generated from AlN during **industrial** processing for sample A and B.
466 **In the** leaching of sample A, methane produced from Al₄C₃ could be **valorised** by burning to
467 **use the thermal energy**.

468

469 Clearly, detailed information of samples acquired by using multiple-scale characterisation
470 methods is key to facilitate the industry to set up appropriate operating parameters and
471 control the hazardous gas generation (**Fig. 6**). It can also reduce unnecessary processing setup
472 **costs** in the industrial salt-leaching recovery process as well.

473

474 5. Conclusions

475

476 Aluminium black dross is a very complex mixture consisting of salts, various metal oxides
477 and a plethora of reactive phases. Moreover, the phases and corresponding volume fractions
478 vary significantly with different industrial and recycled aluminium feed sources. In industry,
479 different toxic gas treatment methods involving aqueous leaching are normally used for
480 recycling salts. A new pre-treatment is presented in this paper, which dissolves the major
481 salt-phases in black dross with glycerol and ethanol. It is seen to be an effective way to assist
482 in determining minor phases.

483

484 In this study, samples A and B from two different industrial sources contained 36 elements in
485 total. Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Br, Sr, Zr, Mo,
486 Rh, Pb, Bi, N, O, Nd were detected in both samples. However, F, Yb, Ba, were only
487 discovered in sample A, while Eu, Se, Cs, and Ce were only observed in sample B. The
488 mineral phases of halite (NaCl), corundum (Al₂O₃), sylvite (KCl), spinel (MgAl₂O₄), quartz
489 (SiO₂), fluorite (CaF₂), cryolite (Na₃AlF₆) and Diaoyudaoite (NaAl₁₁O₁₇) were identified. The
490 existence of amorphous or turbostratic graphitic carbon has been confirmed by Raman
491 spectroscopy. The toxic phase AlN has been identified by XRD, Raman and FTIR. One of
492 the other gas generating phases Al₄C₃ has been, for the first time, detected using FTIR.

493

494 Both the pre-treatment methodology and proposed framework for sample-processing could
495 help in the future remediation and valorisation of black dross waste.

496

497

498 Credit Author Statement

499

500 KH, DR, and MO conceived and designed the study. KH performed the experiments and
501 analysed the data. KH, DR, RS, MO and TR discussed the data. KH and MO drafted the
502 manuscript. KH, MO and TR revised the manuscript. All co-authors approved the final
503 submitted version of the manuscript.

504

505 Declaration of interests

506

507 The authors declare that they have no known competing for financial interests or personal
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509

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518

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