

**Chapter 3:
Preparation of
Hardened pellets from
Multimetallic
Magnetite ore fines
with different Binders**

3.1. Introduction

Pelletization is a pivotal process in the iron and steel industry, converting fine iron ore particles (<4mm) into hardened pellets sized 10-20 mm. These pellets can be easily charged into a blast furnace or electric arc furnace for further ironmaking. This chapter delves into the detailed process of pellet preparation from multimetallic magnetite ore (MMO) fines using four different binders: colemanite, dextrin, carboxymethyl cellulose (CMC), and cornstarch. Each binder's effectiveness was evaluated through the preparation of four sets of pellets per binder, each with varying dosages (0.5 wt.%, 1 wt.%, 1.5 wt.%, 2 wt.%).

The preparation involved mixing MMO with a single binder and moisture in the required proportion. Green pellets were air-dried overnight and oven-dried for 24 hours. Subsequently, the dried pellets were hardened at temperatures ranging from 1000-1250°C to ensure sufficient strength for transportation without degradation. The hardening process of MMO pellets offers two additional benefits beyond achieving optimum strength and porosity. Firstly, it facilitates the conversion of all magnetite to hematite, thereby enhancing the reducibility of the pellets[18]. Secondly, it transforms chromite to a sesquioxide, further improving the pellet's reducibility [79].

This chapter thoroughly examines the essential physical properties of the pellets, encompassing green strength, dry strength, Cold Crushing Strength (CCS), porosity, tumbler index, shatter index, and abrasion index. Notably, pellets bonded with organic binders exhibited superior green strength compared to those bonded with colemanite. However, a contrasting trend emerged in high-temperature properties like CCS, with colemanite-bonded pellets demonstrating better performance. This chapter also describes the characterization of pellets, offering valuable insights into the phase and structural changes occurred during the pelletization process.

3.2. Results and discussion

3.2.1. Visual Observation

Figure 3.1 shows the changes in the appearance of pellets hardened at different temperatures.

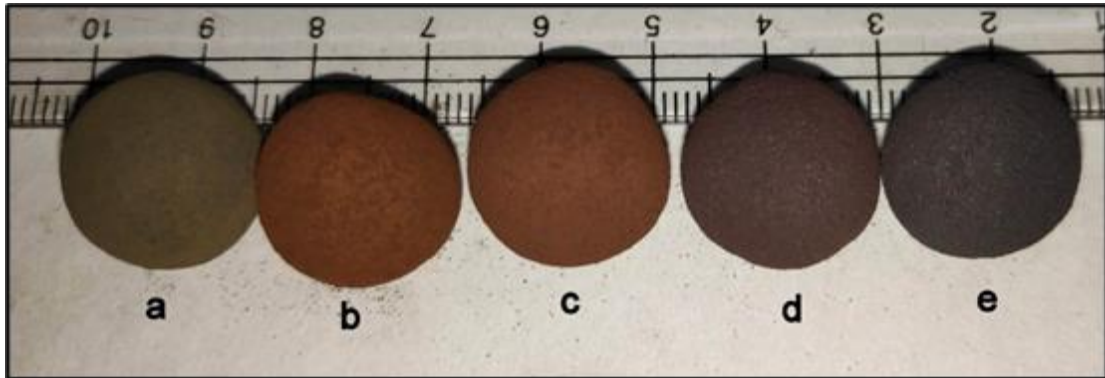


Figure 3.1:(a) Dry pellet; pellet hardened at (b)1000°C (c) 1100°C (d) 1200°C (e) 1250°C

The colour variation observed in the pellet's during firing was attributed to phase changes occurred at different temperatures. Initially, the dry pellets exhibited a dark brown hue (**Figure 3.1a**), which transitioned to reddish-brown at 1000 °C (**Figure 3.1b**) due to the conversion of magnetite to hematite [81]. As the firing temperature increased, the formation of slag bonds within the pellets intensified [16], leading to a darkening of pellets. At 1100 °C, the reddish-brown color changed to brown (**Figure 3.1c**), and further darkened to a deep brown shade at 1200 °C (**Figure 3.1d**), reflecting increased slag bond formation. The highest degree of slag bond formation occurred in pellets hardened at 1250 °C, resulting in a black coloration (**Figure 3.1e**). This colour variation served as a visual indicator of the phase transformations and slag bond development occurred within the pellets during firing.

3.2.2. Green Strength & Dry Strength

Ten pellets per dosage per binder were taken to conduct the drop number test and green strength test. The result of the drop test has been presented in **Table 3.1**. The results of the green strength test and dry strength test are presented in **Figure 3.2**.

Table 3.1: Drop number and green strength of pellets for different binders and dosage combinations

Binder	Property	Dosage (wt.%)			
		0.5	1	1.5	2
Colemanite	Drop number	5	5	5	6
	Green Strength(gm/pellet)	450	550	550	650
	Dry Strength (kg/pellet)	8.15	7.81	7.8	7.85
Cornstarch	Drop number	4	5	5	6
	Green Strength(gm/pellet)	400	450	430	550
	Dry Strength (kg/pellet)	11.3	9.52	9.8	8.46
CMC	Drop number	3	4	4	7
	Green Strength(gm/pellet)	400	450	450	500
	Dry Strength (kg/pellet)	9.12	9.7	12.78	27.56
Dextrin	Drop number	3	4	4	5
	Green Strength(gm/pellet)	300	350	400	470
	Dry Strength (kg/pellet)	12.6	14.14	17.62	21.26

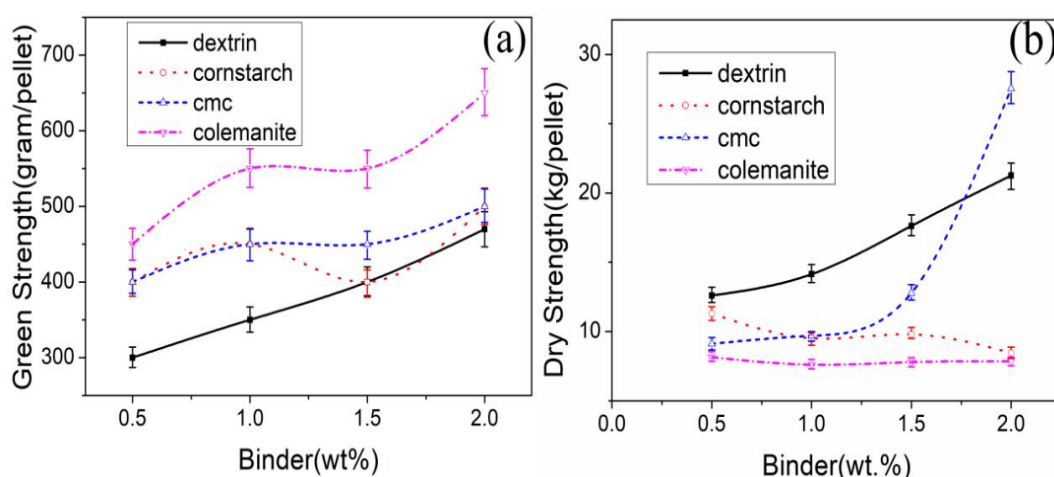


Figure 3.2: (a) Green strength, and (b) Dry strength; for various binder and dosage combinations

The drop number for every binder increased with an increase in dosage (**Table 3.1**).

The green strength of dextrin bonded pellets increased linearly with increase in dosage (**Figure 3.2a**). For other binders, the green strength showed a non-linear increase in

green strength with an increase in dosage. The highest green strength was obtained with colemanite bonded pellets and the highest drop number was obtained with CMC bonded pellets. The overall best green strength properties were therefore obtained with colemanite bonded pellets. The dry strength increased with an increase in dosage for dextrin and CMC bonded pellets, while for colemanite and corn starch bonded pellets, it remained relatively constant (**Figure 3.2b**). Such high strength by dextrin and CMC bonded pellets was due to the presence of a heterocyclic ring and OH⁻ group in its structure. The presence of an aromatic or heterocyclic ring enhances the thermal stability of the binder, and the presence of OH⁻ enhances the wettability of the binder to promote better adhesion between particles [82]. However, all the binders provided dry strength that was well above the industrial standards of 2.2kg/pellet [22, 34, 35].

3.2.3. Cold Crushing Strength (CCS) & Porosity

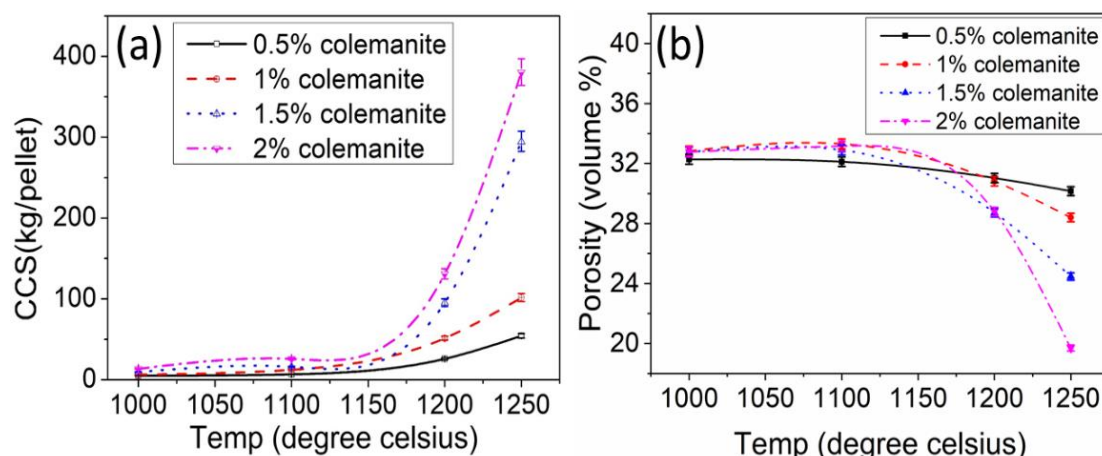
The CCS and porosity of the pellets were determined according to methods detailed in Section 2.5.2 and 2.5.3. The results obtained are described in the following subsections.

3.2.3.1. Colemanite

The porosity and CCS of hardened pellets made with colemanite are given in **Table 3.2**. The variation of porosity and CCS with respect to temperature and binder dosage is shown in **Figure 3.3**. In general, CCS increases and porosity decreases on increasing dosage of binder and firing temperature. It can be seen that CCS bears an inverse relationship with porosity (**Figure 3.3**). The pellets with the highest CCS have the lowest porosity.

Table 3.2: CCS and porosity of colemanite bonded pellets for different dosages

Dosage (wt. %)	Properties	Temperature (°C)			
		1000	1100	1200	1250
0.5	Porosity (vol%)	32.28	32.12	31.04	30.216
	CCS (kg/pellet)	4.89	6.56	25.7	54.19
1	Porosity (vol%)	32.84	33.31	30.82	28.41
	CCS (kg/pellet)	6.2	12.04	51.15	101.562
1.5	Porosity (vol%)	32.76	32.9	28.73	24.47
	CCS (kg/pellet)	9.3	15.87	95.26	294.285
2	Porosity (vol%)	32.78	33.16	28.8	19.7
	CCS (kg/pellet)	13.41	25.73	130.7	379.94

**Figure 3.3:** Variation of (a) CCS, and (b) Porosity; of colemanite bonded pellets with change in dosage

The highest CCS of 379 kg/pellet was obtained, with pellets having 2 wt.% colemanite at a firing temperature of 1250 °C (**Figure 3.3a**). However, the porosity of those pellets was less than 20 vol% (**Figure 3.3b**). Thus, 1.5 wt.% colemanite pellets fired at 1250 °C were deemed better than the 2 wt. % colemanite pellets as the 1.5 wt.% pellets had a CCS of 294 kg/pellet and a porosity of 25 vol%, which were in line with the industrial standards for minimum acceptable CCS requirements (200 kg/pellet) and porosity (>20 vol%) [35, 36].

3.2.3.2. Carboxymethyl cellulose (CMC)

The porosity and CCS of hardened pellets made with CMC are given in **Table 3.3**. The variation of porosity and CCS with respect to firing temperature and binder dosage is shown in **Figure 3.4**.

Table 3.3: CCS and porosity of CMC bonded pellets for different dosages

Dosage (wt. %)	Properties	Temperature (°C)			
		1000	1100	1200	1250
0.5	Porosity (vol%)	32.37	35.75	32.66	29.5
	CCS (kg/pellet)	0.8	1.9	13.9	27.64
1	Porosity (vol%)	33.24	32.15	29.7	28.5
	CCS (kg/pellet)	1.9	4.4	25.2	53.9
1.5	Porosity (vol%)	33.05	31.64	28.2	25.4
	CCS (kg/pellet)	2.46	4.1	32.8	71.72
2	Porosity (vol%)	35	33.05	29.6	24.8
	CCS (kg/pellet)	2.7	6.3	46.5	138.55

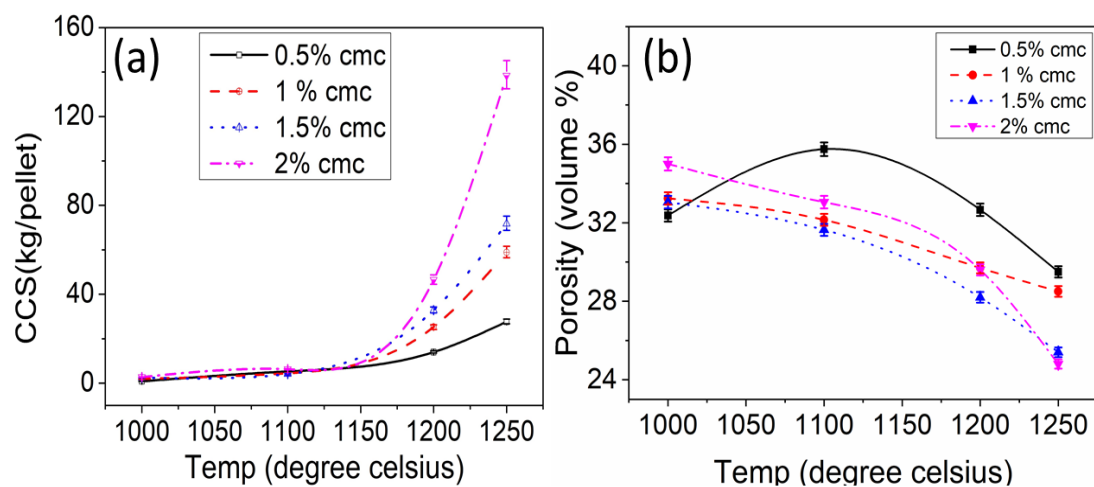


Figure 3.4: Variation of (a) CCS, and (b) Porosity; of CMC bonded pellets with change in dosage

In general, the CCS increased, and the porosity decreased on increasing firing temperature and binder dosage. The highest CCS of 138 kg/pellet was obtained with 2 wt.% CMC at a firing temperature of 1250 °C (**Figure 3.4a**). However, none of the CMC dosages could satisfy the industrial standards of minimum CCS (200 kg/pellet)[22, 36].

3.2.3.3. Cornstarch

The porosity and CCS of hardened pellets made with cornstarch are given in **Table 3.4**.

The variation of porosity and CCS with respect to firing temperature and binder dosage is shown in **Figure 3.5**

Table 3.4: CCS and porosity of cornstarch bonded pellets for different dosages

Dosage (wt. %)	Properties	Temperature (°C)			
		1000	1100	1200	1250
0.5	Porosity (vol%)	32.53	31.96	31.19	30.7
	CCS (kg/pellet)	2.74	4.38	7.3	24.3
1	Porosity (vol%)	34.05	33.85	33.45	32.634
	CCS (kg/pellet)	2.4	4.6	8.4	20.23
1.5	Porosity (vol%)	34.9	33.9	33.86	32.93
	CCS (kg/pellet)	2.19	3.83	8.4	13.65
2	Porosity (vol%)	34.75	35.03	35.48	34.8
	CCS (kg/pellet)	2.4	3.83	6.5	9.3

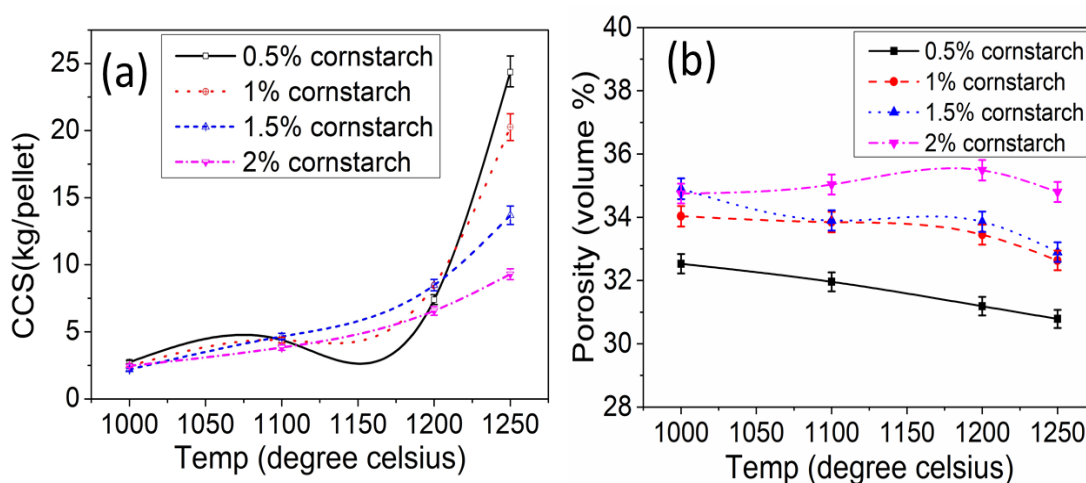


Figure 3.5: Variation of (a) CCS (b) Porosity; of cornstarch bonded pellets with change in dosage

In general, the CCS decreased, and the porosity increased on increasing binder dosage.

The CCS increases, and the porosity decreases slightly on increasing firing temperature.

The highest CCS of 24.3 kg/pellet was obtained with 0.5 wt.% cornstarch at a firing

temperature of 1250 °C. However, none of the pellets could meet the industrial standard of minimum CCS (200 kg/pellet) [36].

3.2.3.4. Dextrin

The porosity and CCS of hardened pellets made with dextrin are given in **Table 3.5**. The variation of porosity and CCS with respect to firing temperature and binder dosage is shown in **Figure 3.6**.

Table 3.5: CCS and porosity of dextrin bonded pellets for different dosages

Dosage (wt. %)	Properties	Temperature (°C)			
		1000	1100	1200	1250
0.5	Porosity (vol%)	31.5	31.8	31.1	30.8
	CCS (kg/pellet)	1.3	4.6	10.1	21.6
1	Porosity (vol%)	32.8	32	31.6	31
	CCS (kg/pellet)	1.3	6.06	8.41	17.24
1.5	Porosity (vol%)	33.6	32.8	31.8	35
	CCS (kg/pellet)	1.09	4.38	7.39	14.23
2	Porosity (vol%)	34	34	35	34.7
	CCS (kg/pellet)	1.09	2.74	3.28	6.3

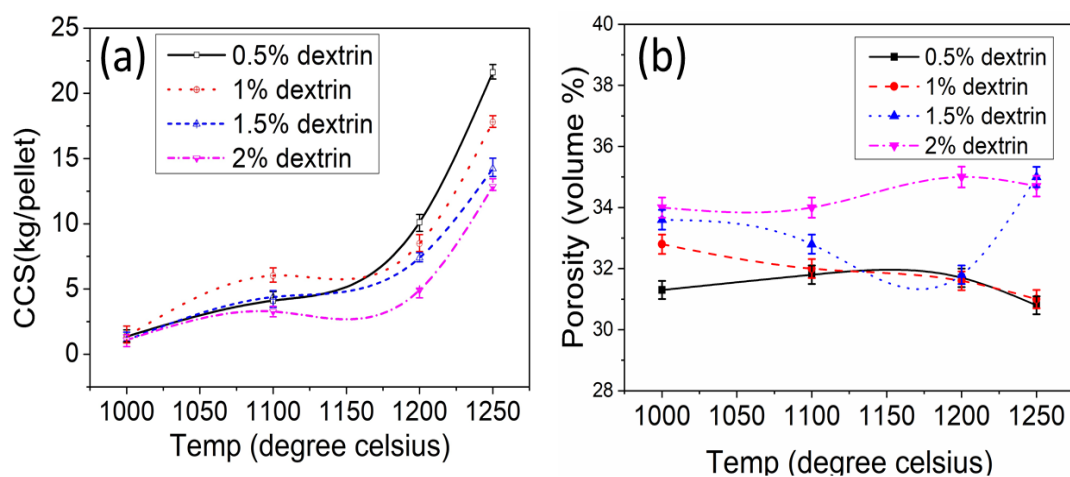


Figure 3.6: Variation of (a) CCS, and (b) Porosity; of dextrin bonded pellets with change in dosage. As was the case with cornstarch bonded pellets, the CCS decreased, and the porosity increased on increasing binder dosage. The CCS increases, but there was not a significant change in porosity on increasing firing temperature (**Figure 3.6b**). The

highest CCS of 21.6 kg/pellet was obtained with 0.5 wt.% cornstarch at a firing temperature of 1250 °C (**Figure 3.6a**). However, none of the pellets could meet the industrial standard of minimum CCS (200 kg/pellet) [14]. Dextrin provided the lowest CCS among all binders.

Based on the literature survey, it was anticipated that the binders would impart the necessary CCS to the pellets. However, it was found that only pellets containing a minimum of 1.5 wt.% colemanite were able to meet the industrial CCS requirement of 200 kg/pellet. The likely explanation for the inadequacy of these binders in providing sufficient CCS lies in its low boiling points. Dextrin, CMC, and cornstarch, for instance, exhibit boiling points below 1000 °C. Consequently, these binders vaporized at the induration temperatures, leaving nothing in the pellets to maintain particle cohesion for final sintering and particle-to-particle fusion. Similar outcomes were reported in other studies as well [22, 32-36] suggesting that adhesion among particles at elevated temperatures had diminished, resulting in reduced sintering and compaction at higher temperatures. This was also the reason for the drop in CCS of dextrin bonded and cornstarch bonded pellets with rise in dosage (**Figure 3.5** and **3.6**). The vaporisation of dextrin and cornstarch led to the creation of voids inside the pellets which increased with rise in dosage. On the other hand, Colemanite, with its melting point of approximately 986 °C, was effective in ensuring particle adhesion at induration temperatures of > 1200 °C [83].

Moreover, it was observed that there was a sudden rise in CCS from 97 kg/pellet to 298 kg/pellet, with a change in firing temperature from 1200 °C to 1250 °C for 1.5 wt.% colemanite pellets (**Figure 3.3a**). Thus, it was imperative to determine the phase and morphological changes that could have led to the high CCS values.

3.2.4. Phase Analysis

XRD analysis of three samples, one each for 1.5 wt.% colemanite bonded dry pellet, 1.5 wt.% colemanite bonded pellet fired at 1200 °C and 1.5 wt.% colemanite bonded pellet fired at 1250 °C, was done to determine any phase changes during induration, which is shown in **Figure 3.7**.

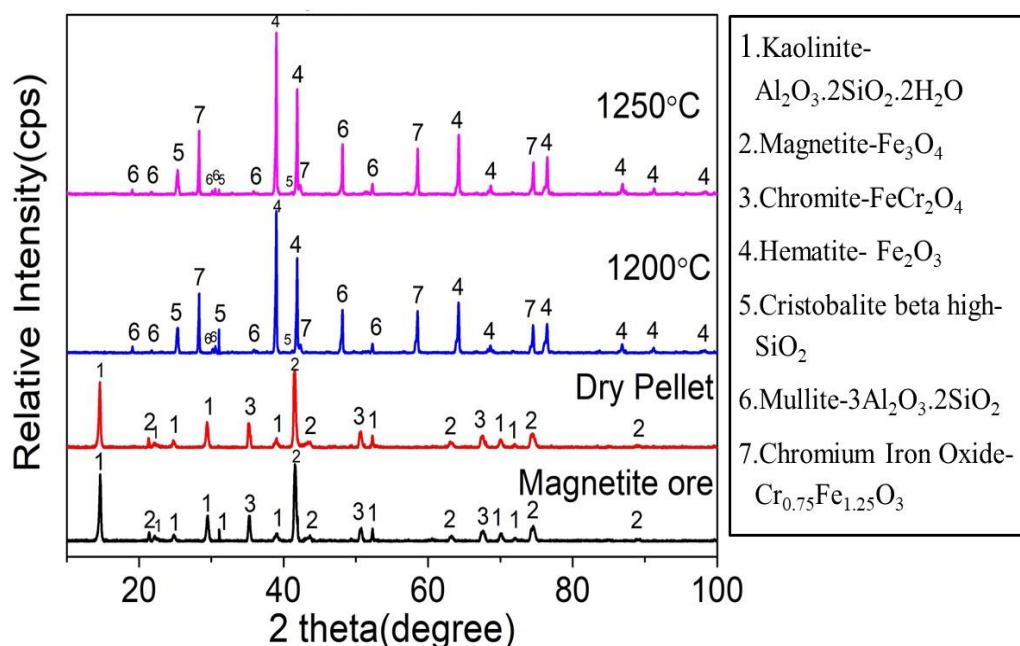


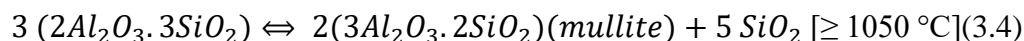
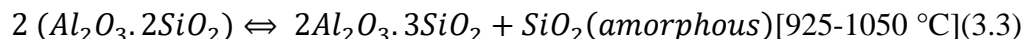
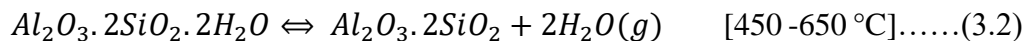
Figure 3.7: XRD analysis of pellets containing 1.5 wt.% colemanite

From **Figure 3.7**, it is evident that only three phases are present in the ore, i.e., magnetite, kaolinite, and chromite. No phase change was observed in the dry state. However, a phase change was observed during hardening at a temperature of 1200 °C. All the magnetite had completely changed into hematite. A similar type of result was observed by Yang [84] at a temperature of 1100 °C. The phase change from magnetite to hematite could be one reason for the strengthening of pellets as this transformation leads to diffusion of Fe^{3+} and rearrangement of Fe_2O_3 crystal lattices, which results in a compact microstructure [85]. At 1250 °C, similar phases were observed, and the intensity of the hematite phases, in general, was found to increase. The phase changes are explained as below.

- Magnetite to hematite [84, 86]



- Kaolinite to mullite and sillimanite [87]



- Chromite to Chromium Iron Oxide [88]

This conversion can be understood from the phase diagram shown in **Figure 3.8**.

3.8.

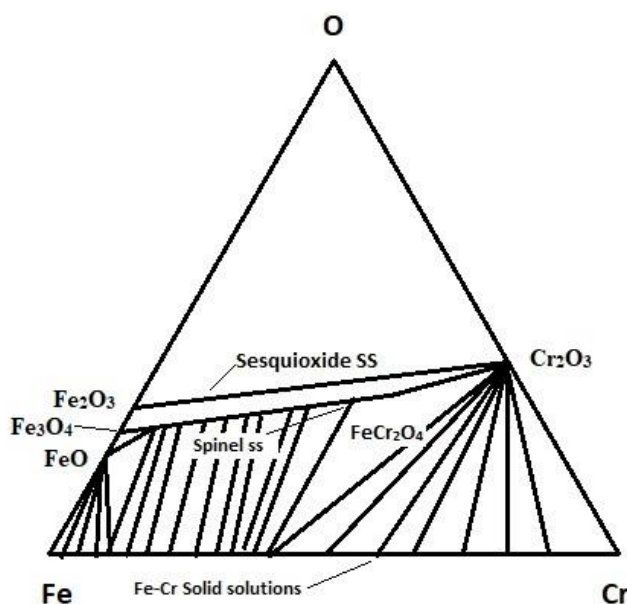


Figure 3.8: Fe-Cr-O phase diagram (adapted from Levin et al) [88]

As it can be seen from the phase diagram, that at higher oxidation levels FeCr₂O₄ changes to a sesquioxide solid solution. **Sesquioxide** is an oxide containing three atoms of oxygen with two atoms (or radicals) of another element(s). For example, aluminum oxide (Al₂O₃) is a sesquioxide. Cr_{0.75}Fe_{1.25}O₃ is a

sesquioxide since 3 atoms of oxygen are combined with a sum total of 2 atoms comprising of Cr and Fe.

It can be observed from the XRD data, that there was no change in phases between the pellet fired at 1200 °C and the pellet fired at 1250 °C (**Figure 3.7**). The phases were similar with a minor increase in the intensity of the phases in the XRD pattern of the pellet fired at 1250 °C. Thus, the transformation of magnetite to hematite could not be the only reason for the drastic increase in CCS and the strength change could be due to sintering of grains.

3.2.5. Morphology Analysis

SEM analysis was conducted on two samples: one comprised of pellets containing 1.5 wt.% colemanite fired at 1200°C, and the other with the same colemanite concentration

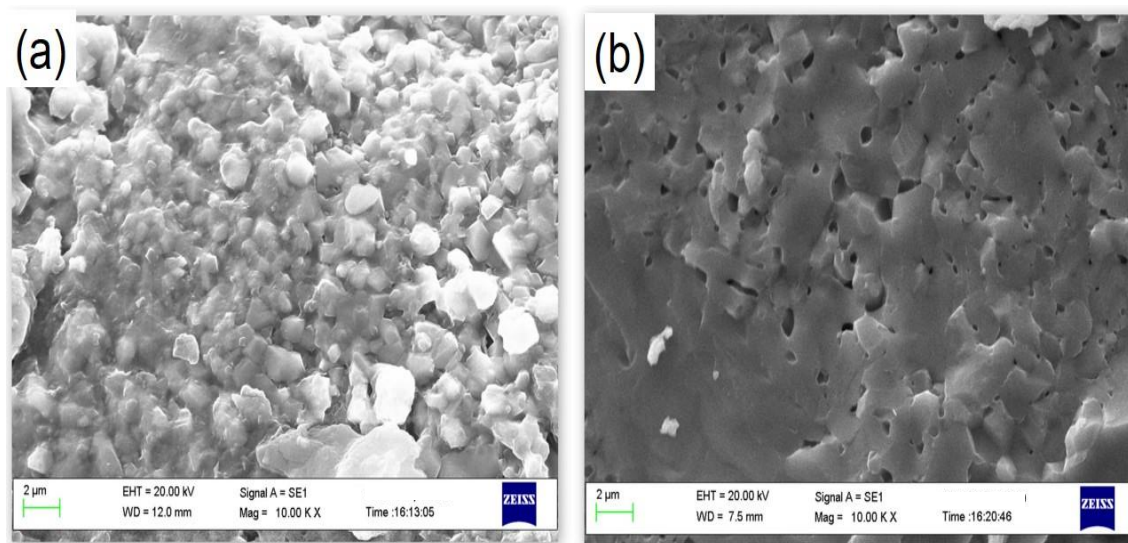


Figure 3.9: SEM images of MMO pellets with 1.5 wt.% colemanite hardened at (a) 1200 °C; and (b) 1250 °C

fired at 1250°C. The purpose was to examine the morphological alterations in the pellets. **Figure 3.9** displays the SEM images for comparison.

In **Figure 3.9a**, individual grains are discernible, with a noticeable transformation into a globular shape. This globular structure observed at 1200 °C signals the onset of sintering, typically characterized by particle-to-particle fusion, wherein grain boundaries melt, leading two particles to merge into one[81, 83]. **Figure 3.9b** depicts

a surface that is fully sintered, with significantly reduced blank spaces. The appearance suggests that the particles melted and fused upon cooling. Notably, particle-to-particle sintering and substantial strength enhancement typically commence only after reaching temperatures of 1200 °C [16]. Hence, this observed sintering process was the primary factor contributing to the drastic alteration in CCS upon increasing the firing temperature.

The combined effect of binders and temperature can be seen in the hardening behavior of multimetallic magnetite ore fines. The temperature effect is only visible with colemanite as it is the only binder that does not vaporise at such high temperatures and is able to hold the particles together in close proximity for sintering to take place. Other binders vaporise at close to 900 °C and so the particles in the pellets are loosely held at a sintering temperature of 1250 °C. Therefore, from the above results, it can be reasonably established that high firing temperature along with the usage of a non-acidic, low melting point, high boiling point binder is the primary requirement for the hardening of MMO pellets.

3.2.6. Shatter, tumbler and abrasion tests

Based on the findings from previous sections, it was determined that pellets bonded with 1.5 wt.% colemanite and fired at 1250 °C exhibited superior characteristics. Consequently, to evaluate its suitability for handling and transportation; shatter, tumbler, and abrasion tests were conducted. These tests aimed to assess the pellets' resistance to breakage, their ability to withstand tumbling during transportation, and their resistance to wear caused by handling and transport. The procedures for these tests have been detailed in section 2.5.4. **Table 3.6** shows the details of the tumbler, shatter and abrasion tests.

Table 3.6 : Particulars of the shatter and tumbler tests

Wt. of sample for shatter test	5 kg
Wt. of sample retained on 10 mm sieve	4.96 kg
Shatter Index	99.2 %
Wt. of sample for abrasion and tumbler test	5 kg
Wt. of sample retained on 6.3 mm sieve	4.76 kg
Tumbler Index	95.35%
Wt. of sample passing through 0.5 mm sieve	0.21
Abrasion Index	4.2%

From the above results, it was established that the SI, AI and TI for the 1.5 wt% colemanite bonded pellets satisfied the industrial requirements (**Table 1.1**).

3.3. Conclusions

Pelletization behaviour of MMO fines with four different binders (colemanite, dextrin, cornstarch and carboxymethyl cellulose) were investigated and the following conclusions are drawn:

- Sufficient green strength and dry strength were obtained with all the binders, i.e., colemanite, dextrin, cornstarch and carboxymethyl cellulose (CMC).
- A high firing temperature coupled with a nonacidic, low melting point, and high boiling point binder like colemanite was necessary for the pellets made from this MMO to achieve industrially acceptable CCS values.
- Pellets made with 2 wt.% colemanite and hardened at 1250 °C gave the best CCS of 379 kg/pellet, but its porosity was extremely low (19 vol.%). Thus, the most optimum binder dosage and induration temperature was fixed to be 1.5 wt.%

colemanite and 1250 °C, respectively, as it provided sufficient CCS of 297 Kg/pellet and a porosity of 25 vol.%.

- The 1.5 wt.% colemanite bonded pellets showed a Tumbler Index of 95.35%, Shatter Index of 99.2 %, and Abrasion Index of 4.23 %. It confirms that not much dust will be generated during handling and transportation of the hardened pellets.
- Sintering and transformation of magnetite to hematite were observed to be the chief causes of high CCS values (>200kg/pellet) in 1.5 wt.% colemanite bonded pellets.