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Study on condition prediction and influencing factors of manganese carbonate recovery by high gradient pulse magnetic separation

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Abstract: Manganese carbonate ore belongs to weakly magnetic minerals, and its co-associated minerals are mainly non-magnetic minerals, which can be separated from gangue minerals at high magnetic field intensity. However, manganese grade and recovery of magnetic separation concentrate of manganese carbonate ore are low in actual production. Therefore, the influences of manganese carbonate particle size, magnetic field intensity, volume susceptibility, pulse stroke, pH, and other factors were studied. The optimal test conditions for manganese carbonate ore recovery by high-gradient magnetic separation were predicted through the calculation results. The results show that the particle radius of manganese carbonate is 0.020 mm, the pulse impulse time is 200 r/min, and the magnetic field intensity is 0.9 T. The optimum condition test was carried out with Qianbei manganese carbonate ore as the material. The test results show that the optimum conditions are the particle radius of 0.074-0.019 mm, pulse impulse time of 200 r/min, and magnetic field intensity of 1.2 T. The reason for the deviation is that the actual ore has a fine distribution particle size, many associative bodies, complex composition, and serious agglomeration, resulting in variable particle volume susceptibility. The capture yield increases with the increase of magnetic field intensity and volume susceptibility but decreases with the increase of pulse. The lower the surface potential of manganese carbonate, the higher the recovery of manganese carbonate. The grade of manganese concentrate was 19.06% and the recovery was 76.85%. Mixed manganese concentrate with a grade of 18.04% and recovery of 87.14% was obtained by adding drugs and changing the grinding method.

Keywords: mineral particles, impulse, volume susceptibility, magnetic field strength, DLVO theory

1. Introduction

The experimental manganese carbonate ore was collected from a certain manganese carbonate ore in northern Guizhou. Manganese carbonate ore belongs to weakly magnetic minerals, while gangue minerals are mainly non-magnetic minerals. It is possible to select high gradient pulse magnetic separation to recover manganese carbonate ore according to its specific magnetization coefficient. The ore is sorted in a magnetic separator using external magnetic field force, water flow impulse force, and pulse competitiveness. Under these forces, the magnetic field force acting on the magnetic particles is greater than the competitiveness, and they are adsorbed onto the magnetic medium. The competitiveness of nonmagnetic particles is greater than the magnetic field force, which is washed away by water flow, thus achieving the separation effect. The working principle of the high gradient magnetic separator is shown in Figs. 1-a, 1-b, and 1-c（Xiong et al., 1998).

Zhang et al. (2018) conducted a "one coarse and one sweep" high-intensity magnetic separation operation on the raw ore with an Mn grade of 9.52% and obtained a concentrate Mn recovery of 85.54% and a grade of 15.56%. Tang and Que (2017) and others adopted the strong magnetic separation process of "one coarse, two fine and one sweeping closed circuit" for low-grade rhodochrosite with a grade of 7.34%, and obtained a magnetic separation concentrate with a recovery of 81.11% and a grade of 17.24%. Pan and Liu (2016) conducted a laboratory small-scale closed-circuit high-intensity magnetic separation experiment and an expanded continuous experiment on a low-grade manganese carbonate ore with a grade of 7.14% in Guangxi, obtaining a magnetic separation concentrate with a grade of 15.53% and a

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recovery of 77.79%, and a magnetic separation concentrate with a manganese grade of 15.57% and a recovery of 76.18%, respectively. Zhang et al. (2016) used the roasting magnetic separation process for low-grade manganese ore with a grade of 8.77%, resulting in a concentrate index of 11.69% and a recovery of 36.74%. Zou et al. (2014) and others used new collectors QY, sodium silicate, and sodium hexametaphosphate as depressants and dispersants of gangue minerals such as quartz and calcite for rhodochrosite with a grade of 12.35%, and adopted the flotation closed circuit process of "one coarse, three fine, two sweeps and sequential return of middlings" to obtain a flotation concentrate with a grade of 16.92% and a recovery of 85.13%. The above research shows that the rhodochrosite beneficiation method has a complex process flow, high cost, and poor concentrate beneficiation index. Xiong (2002) used SLON vertical ring pulse high gradient magnetic separator to conduct a magnetic separation test for Meishan hematite, siderite (Xiong et al., 1994), Gushan iron ore (Xiong et al., 2000), Qidashan hematite (Xiong et al., 2002), Donganshan hematite (Xiong et al., 2003) and other concentrators, and finally these weak magnetic minerals can reach the recovery index. Manganese carbonate ore also belongs to weakly magnetic minerals. Therefore, this study chooses to use calculation methods to first predict the high gradient magnetic separation recovery conditions of manganese carbonate ore, and then conduct magnetic separation tests on the actual ore of manganese carbonate ore. The analysis of the difficulty in improving the grade and recovery of concentrate products during the high gradient magnetic separation process of manganese carbonate ore, as well as the situation of manganese tailing in tailings, explores the optimal magnetic separation conditions of manganese carbonate and provides corresponding references for the magnetic separation recovery of actual manganese carbonate ore.

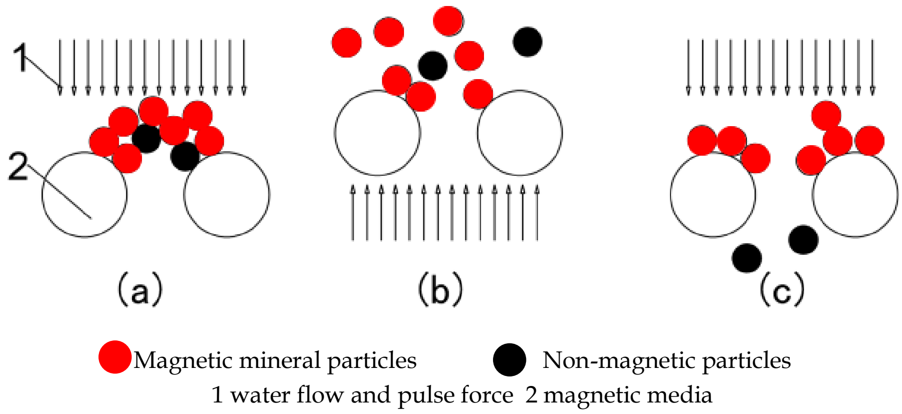

Fig. 1. Theoretical acquisition of magnetic minerals in a pulsed high-gradient magnetic separator

2. Ore property analysis

2.1. Analysis of chemical elements in ores

The content of chemical elements in ore was determined by X-ray fluorescence spectrometry and the analysis results are presented in Table 1.

Table 1. Ore (XRF) chemical element analysis (%)

Mn	TFe	BaO	CaO	Cr_2O_3	K_2O	MgO	Al_2O_3
12.82	3.26	0.06	5.37	0.02	2.26	2.06	10.41
SiO_2	SO_3	SrO	TiO_2	ZnO	Na_2O	P_2O_5	LOI 1000
35.20	4.74	0.04	0.34	0.02	0.99	0.59	19.06

As seen from Table 1, the manganese grade in the ore is 12.82%, Mn/Fe ratio 3.93, P/Mn ratio 0.02, S/Mn ratio 0.15, Mg/Ca ratio 0.32, and magnesium oxide content is 2.06%, which belongs to high iron, high phosphorus, high sulfur, high silicon, and high clay manganese carbonate ore. Gangue mineral elements are mainly Ca, K, Mg, Al, and Si elements.

2.2. Mineral composition analysis

X-ray diffraction (XRD) was used to analyze the mineral composition of the ore, and the analysis results are shown in Fig. 2. As shown in Fig. 2, the XRD quantitative analysis results show that the ore is mainly composed of manganese carbonate ore, quartz, plagioclase, calcite, siderite, pyrite, dolomite, gypsum, and kaolinite.

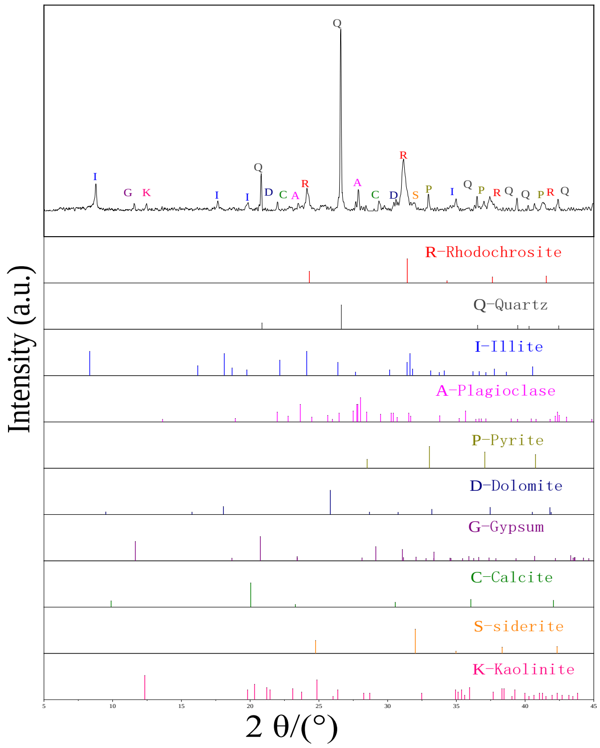

Fig. 2. XRD analysis map of ore mineral composition

2.3. Study on distribution characteristics and isomorphism of minerals

As can be seen from Fig. 3, manganese carbonate ore exists in the mud aggregate structure. Dolomite and pyrite are found in the grains of manganese carbonate ore. Part of manganese carbonate ore is produced as granular aggregate, and the other part is produced as banded aggregate. Locally, several clumps can be seen distributed in bands.

As can be seen from Fig. 4, in the presence of mutual doping between manganese carbonate ore and dolomite, the isomorphism among Ca, Mg, and Mn is serious. There are elements Mn in dolomite and Ca and Mg in manganese carbonate ore.

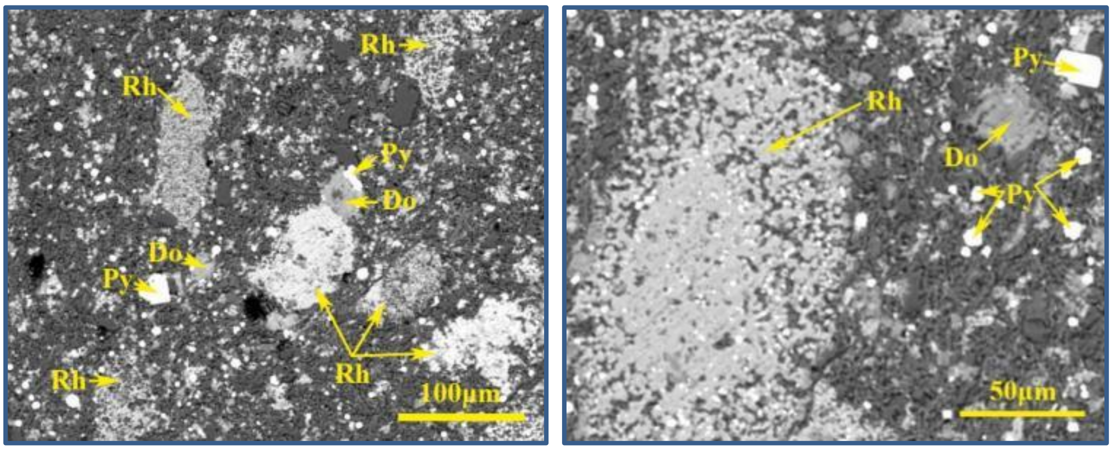

Fig. 3. Analysis of manganese carbonate characteristics. Rh: rhomonite; Do: dolomite; Py: pyrite

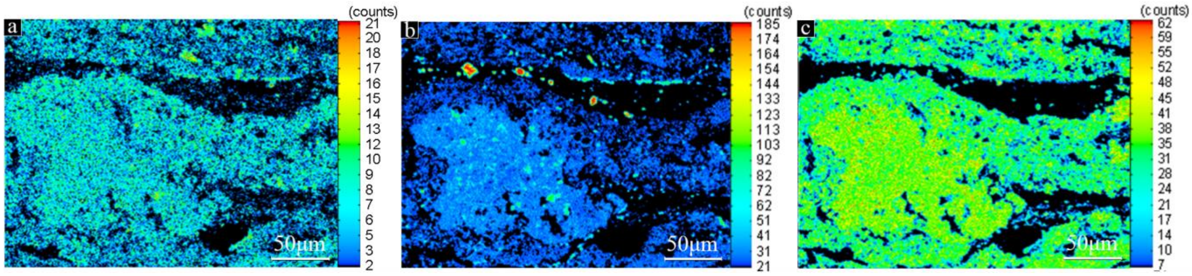

Fig. 4. Scanning analysis of manganese carbonate, a: Mg element scan; b: Ca element scan; Mn: element scan

3. Calculation and prediction of magnetic separation and recovery conditions for manganese carbonate ore

3.1. Calculation of P and analysis of influencing factors based on a single-layer magnetic medium

Manganese carbonate ore belongs to weak magnetic minerals, which are jointly acted by water flow impulse, impulse force F1, gravity F2, viscous force F3, and magnetic force Fm in the process of high gradient magnetic separation. As shown in Fig. 5, the separation of magnetic and non-magnetic particles is determined by magnetic Fm and competitive force FC. Only the interaction between manganese carbonate particles and magnetic medium is considered, and the electrostatic force and Van der Waals between mineral particles on magnetic medium and mineral particles in pulp are not considered. The probability P of mineral particles being captured through a single magnetic medium is approximately proportional to the magnetic force and inversely proportional to the competitiveness, which is the sum of water impulse force, impulse force F1, gravity F2, and viscous force F3. The formula for calculating probability P is shown as formula (Xiong et al., 1989; Xiong et al., 1998; Zhang et al., 2019) (2).

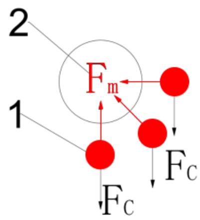

Fig. 5. Power map of magnetic separation particles in the pulp. 1: Magnetic mineral particles; 2: magnetic media; F_C competitiveness; Fm magnetic force

$$\mathrm{F_C}=F_1+F_2+F_3 \tag{1}$$

$$F_1=\frac{\pi}{5}\mu\mathrm{SN}+\frac{\pi}{900}\mathrm{mSN}^2$$

$$F_2=\mathrm{mg}$$

$$F_3=6\pi\mu a v_0$$

$$\mathrm{F_m}=\frac{8\pi^2}{3}\mathrm{a}^3\kappa\mathrm{H}\frac{\mathrm{M_{sf}}}{\mathrm{d_0}}$$

$$\mathrm{P}=\mathrm{K}\frac{\mathrm{F_m}}{\mathrm{F_C}}=\mathrm{K}\frac{\frac{8\pi^2}{3}\mathrm{a}^3 X\mathrm{H}\frac{\mathrm{M_{sf}}}{\mathrm{d}}}{6\pi\mu a v_0+\mathrm{mg}+\frac{\pi}{5}\mu\mathrm{SN}+\frac{\pi}{900}\mathrm{mSN}^2} \tag{2}$$

where P — collection probability, Fm — magnetic force, F_C — Competitiveness, K — proportionality constant, X — particle volume susceptibility, H — background field strength, M_{sf} — Magnetization of magnetic media, d — radius of the magnetic medium, μ — viscosity coefficient, v_0 — feed rate; S — pulse stroke, N — pulse stroke, a — particle radius, F_1 — impulse force, F_2 — gravity, F_3 — viscosity.

According to the calculation formula given above, the high gradient magnetic separation test conditions of the manganese carbonate ore were tentatively predicted, and the single-layer magnetic medium capture yield was calculated by taking the ore particles below the magnetic medium as the object. When mineral particles and magnetic media are shown in Fig. 5. Setting mineral conditions $a=1\times10^{-3}$ cm, $X=200\times10^{-6}$ cm^3/g; H=1.2 T; $d=2.5\times10^{-3}$ cm; $\mu=0.8973$; $v_0=3$ cm/s, $S=0.6$ cm.

Selection of mineral particle size, mineral volume susceptibility, external magnetic field intensity, and pulse times, respectively, influence on P. Discuss the experimental conditions for magnetic separation of manganese carbonate ore to recover manganese metal using three calculation results, as shown in Figs. 6-8.

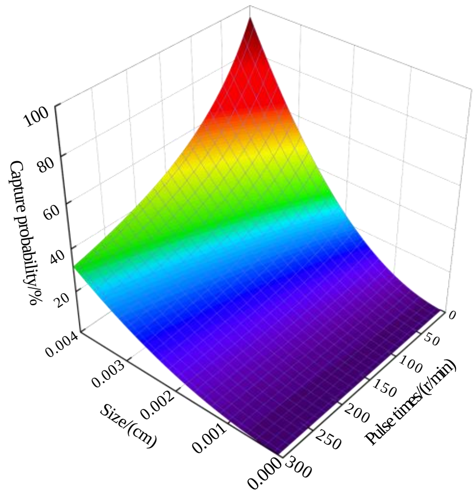

Fig. 6. Effect of mineral particle size and impulse interaction on P

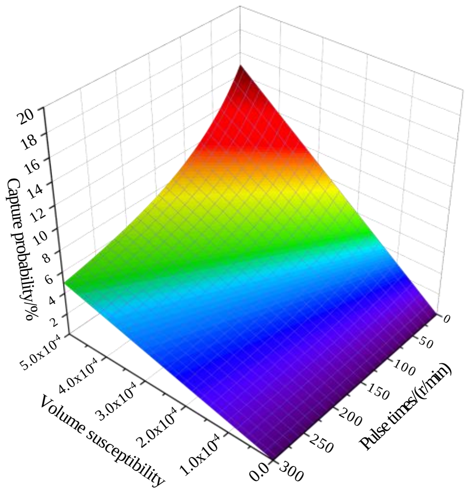

Fig. 7. Mineral volume susceptibility and impulse interaction effect on P

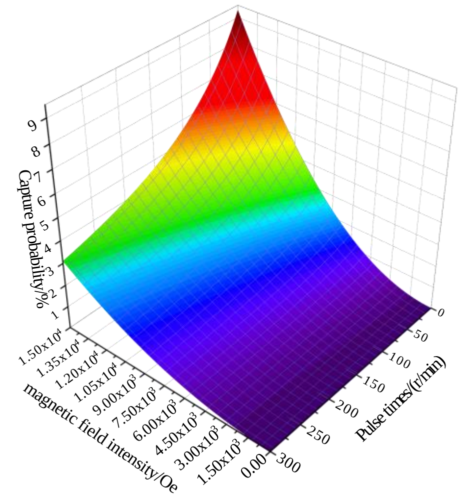

Fig. 8. The mutual influence of external magnetic field strength and impulse on P

As shown in Fig. 6, the particle size has a significant impact on the capture rate during the magnetic separation recovery process. It can be seen that the capture rate of single-layer magnetic media on manganese carbonate particles increases with the increase of radius. Compared to the influence of particle radius of manganese carbonate ore, the impact of pulse on fine-grained particles is worse than that of coarse-grained particles. When the radius of manganese carbonate particles is below 0.020 mm, the capture rate mainly depends on the particle radius, and the pulse has little effect on it. The main reason is that the radius of mineral particles is a cubic function of the magnetic force exerted on manganese carbonate in a high-gradient magnetic separator. Based on the calculation results, a particle radius of 0.002 mm is used as the optimal magnetic separation particle size for manganese carbonate ore. The effect of pulse on the capture rate is relatively small when it is less than 200 r/min. After reaching 200 r/min, increasing the pulse results in a small trend in the capture rate. Therefore, it is initially determined that the optimal condition is a pulse of 200 r/min. It can be seen from Fig. 7 that when the high gradient pulse magnetic separator recovers manganese carbonate ore, the single layer magnetic medium's capture rate of manganese carbonate ore particles is proportional to the magnetic susceptibility of the particle volume. With the increase of particle volume susceptibility, the capture rate also increases. The liberation of manganese carbonate ore needs to avoid the phenomenon of sliming and agglomeration caused by continuous grinding. The actual composition of manganese carbonate ore is complex, and gangue minerals are mainly non-magnetic minerals. The formation of agglomeration will affect its volume susceptibility, resulting in difficulty in recovery. The experiment also shows that a pulse of 200 r/min is the optimal magnetic separation condition. As shown in Fig. 8, the capture rate of manganese carbonate particles by a single-layer magnetic medium is positively correlated with the magnetic field intensity of the magnetic separator. After the magnetic field intensity reaches 0.9 T, under lower pulse magnetic separation conditions, the capture yield line is steep, but below the magnetic field intensity of 0.9 T, the pulse is difficult to have an impact on the capture yield, making it a device. Therefore, the optimal condition for determining the experimental magnetic field intensity to be 0.9 T is determined. The results of three calculations show that the magnetic separation of manganese carbonate ore with a pulse rate of 200 r/min can achieve dispersion without causing pulse as the main influencing factor. After calculation, it is predicted that the optimal magnetic separation conditions are the particle radius of 0.020 mm, magnetic field strength of 0.9 T, and pulse rate of 200 r/min as the optimal conditions.

3.2. Calculation of multilayer magnetic adsorption interaction potential energy of manganese carbonate based on EDLVO theory

As shown in Fig. 9, when a layer of magnetic mineral particles is formed on the surface of the magnetic medium, it is difficult for the magnetic medium to capture the magnetic mineral particles in the slurry compared to the initial magnetic medium. In addition to the shear force of the fluid on mineral particles, there is a repulsive effect of electrostatic force Fh between homogeneous mineral forces, which increases competitiveness and reversely reduces the effect of magnetic force, resulting in a decrease in capture efficiency. In the process of high gradient pulse magnetic separation, not only magnetic particles are captured by the surface of the magnetic medium, but also magnetic attraction is needed to form multi-layer capture. The agglomeration and dispersion of particles are controlled by a variety of forces. Under the condition of a high gradient pulsed external magnetic field, the interaction energy VT is calculated as Eq. 3 (Wang et al., 1993):

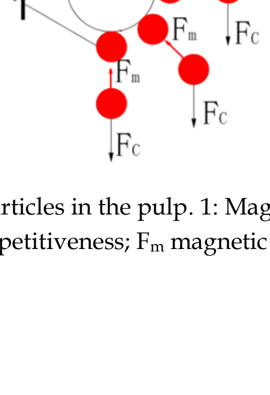

Fig. 9. Power map of magnetic separation particles in the pulp. 1: Magnetic mineral particles; 2: magnetic media; F_C competitiveness; F_m magnetic force

$$V_T = V_W + V_E + V_M + V_H \tag{3}$$

Van der Waals force interaction energy between manganese carbonate particles:

$$V_W = -\frac{A}{6}\left[\frac{2a^2}{4ax+x^2} + \frac{2a^2}{(2a+x)^2} + ln\frac{4ax+x^2}{2a+x^2}\right]$$

The electrostatic interaction energy between manganese carbonate particles:

$$V_E = 4\pi\varepsilon a^2\varphi^2\frac{e^{-kx}}{2a+x}$$

Magnetic dipole polarization interaction energy between manganese carbonate particles:

$$V_M = -\frac{8\pi\mu_0 X^2H^2a^6}{9(x+2a)^3}$$

Shear energy of manganese carbonate particles:

$$V_H = -\frac{\pi^2a^2}{4}b\rho^{\frac{1}{2}}v^{\frac{1}{2}}\mathcal{J}^{\frac{1}{2}}(x+2a)^{-\frac{1}{2}} \times (9.861\theta - 3.863\theta^3 + 0.413\theta^5)$$

The magnetic dipole polarization interaction energy between manganese carbonate particles and magnetic media (calculated based on the formula proposed by J. Svoboda):

$$V_T = -\frac{\mu_0 X}{2}\left\{\frac{4\pi MHa^3}{3(1+a/b)^2} + \frac{\pi M^2a^3}{4(1+2a/b)}\left[\frac{a}{b} + \left[\frac{(a/b)^2}{(1+2a/b)^{\frac{1}{2}}} - (1+2a/b)^{\frac{1}{2}}\right]arctan\frac{a/b}{(1+2a/b)}\right]\right\}$$

In the formula, V_T—total potential energy, V_W— van der Waals interaction potential energy, V_E—double layer interaction energy, V_M— magnetic dipole polarization interaction energy, V_H— fluid shear interaction energy (fluid shear interaction energy in high gradient pulse magnetic separators includes shear interaction energy generated by water flow impulse and shear interaction energy generated by pulse). H—magnetic field intensity, A— Hamak constant, k—Debye Hooker parameter, b—magnetic medium radius, X—manganese carbonate particle volume susceptibility, ε—slurry dielectric constant, φ — particle surface potential, x — mineral particle distance, μ_0 — vacuum permeability, a — mineral particle radius, M—magnetic medium magnetization,v—slurry flow rate and pulse action speed, ρ—Fluid density, $\mathcal{J}$— slurry viscosity, θ— The angle between the front stagnation point and the direction of flow velocity. During the magnetic separation process, there are two types of agglomerations formed between manganese carbonate particles: 1. Manganese carbonate particles agglomerate in the slurry; 2 Manganese carbonate particles agglomerate on the surface of magnetic media. The interaction energy between manganese carbonate particles in pulp, the interaction energy between manganese carbonate particles and magnetic medium, and the interaction energy between magnetic medium and manganese carbonate ore in the pulp after magnetic adsorption of a layer of manganese carbonate ore. Predict the pH of the slurry and re-determine the pulse, magnetic field intensity, etc.

When recovering manganese carbonate ore through high gradient pulse magnetic separation, the formation of homogeneous agglomeration of fine manganese carbonate particles in the slurry can increase the volume of manganese carbonate particles, thereby increasing the probability of magnetic medium capturing manganese carbonate. In the magnetic separation process of manganese carbonate ore, there is not only van der Waals force and electrostatic force between particles, but also magnetic force between weakly magnetic particles of manganese carbonate in the magnetic field. In a high gradient pulse magnetic separator, the slurry flow rate is relatively small, and during the magnetic separation process, the ore particles are synchronized forward. The relative motion speed between the manganese carbonate particles in the slurry is zero, and the fluid shear stress energy is equal to zero. When there is relative motion between mineral particles in the slurry and existing mineral particles in the magnetic medium, the shear energy of the water flow impulse and pulse on it cannot be ignored. The potential energy of double layer interaction and van der Waals potential energy can be calculated based on the EDLVO theory (there is electrostatic force between mineral particles in the slurry and between mineral particles in the slurry and mineral particles on the magnetic medium). Three forms of interaction energy of manganese carbonate particles in the magnetic separator are calculated respectively, and the calculation results are shown in Figs. 10-12. Hamaker constant of manganese carbonate A=7.05× 10^{-14} erg, water Hamaker constant A=3.5× 10^{-14} erg, b=2.5 × 10^{-3} cm, X=200× 10^{-6} cm^3/g, ε = 78.54, a=1×10^{-3} cm.

As shown in Fig. 10, due to the repulsive effect of isotropic charges between manganese carbonate particles, the potential energy barrier gradually increases as the surface potential of manganese carbonate increases. When φ= At 10 mV, the potential energy decreases and disappears. Between -10 mv and +10 mV, manganese carbonate ore is prone to homogeneous condensation. Therefore, the

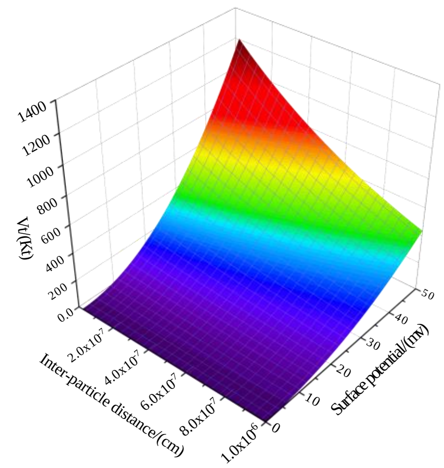

Fig. 10. The interaction energy between the homogeneous particles of manganese carbonate

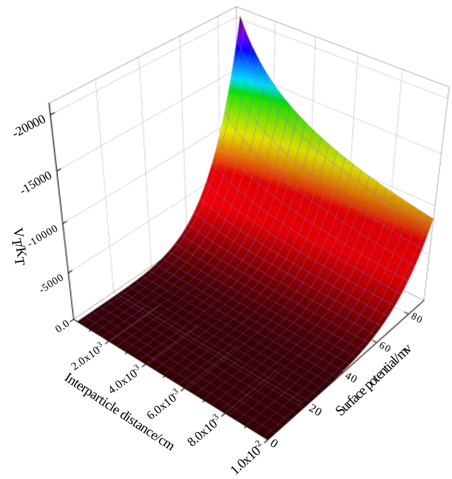

Fig. 11. Calculation of the interaction energy between the manganese carbonate particles and the magnetic medium in the pulp

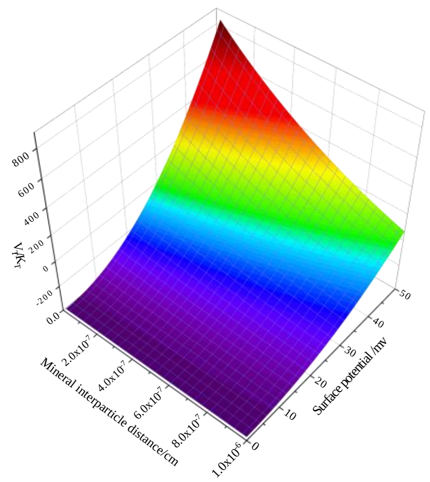

Fig. 12. Interaction energy between manganese carbonate particles and magnetic medium

surface potential of manganese carbonate ore is used to determine the pH value of the slurry. As shown in Fig. 11, the attraction between manganese carbonate particles and magnetic media in the slurry increases with the increase of the angle between the front stagnation point and the direction of flow velocity, and the interaction attraction also increases. Compared to the mutual aggregation of manganese carbonate particles in mineral pulp, the magnetic adsorption of manganese carbonate particles on magnetic media is much easier. When the angle between the front stagnation carbonate particles on magnetic media is much easier. When the angle between the front stagnation point and the flow direction is less than 40^o, manganese carbonate particles can effectively magnetically adsorb on the magnetic media, enabling effective recovery of manganese carbonate particles. As shown in Fig. 12, as the surface potential of manganese carbonate particles increases, the potential energy barrier gradually increases. When the surface potential of manganese carbonate is between -30 mV and +30 mV, the potential energy barrier does not exist. Manganese carbonate particles in the mineral pulp can form multi-layer adsorption on the surface of magnetic media, which is much more difficult to form compared to the magnetic adsorption of manganese carbonate particles and magnetic media. When the surface potential of manganese carbonate ranges from -30 mV to + 30 mV, the force between manganese carbonate particles in the slurry and magnetic medium surface particles is gravitational. It is much easier to agglomerate between manganese carbonate particles in ore slurry. Compared to the pH value of the slurry in Fig. 10, the pH value of the slurry can be expanded when forming multi-layer adsorption.

4. Test plan and method

The phenomenon of using a high gradient pulse magnetic separator for the actual recovery of manganese carbonate ore is shown in Figs. 13a-c. Figure 13-a shows the recovery state of manganese carbonate ore without pulse conditions, where various gangue minerals and partially dissociated particles are mixed in the magnetic medium. Figure 13-b shows the recovery state of manganese carbonate ore under small pulse conditions, with particles mainly composed of gangue minerals being competitively separated. Small pulses can significantly improve the quality of the concentrate. Figure 13-c shows the recovery state of manganese carbonate ore under high pulse conditions. Under these conditions, some large particles mainly composed of manganese carbonate and fully cleaved manganese carbonate particles are competitively removed from the magnetic medium. Under high pulse conditions, the concentrate grade can be effectively increased, but the manganese recovery will decrease. Therefore, the following studies are conducted on the manganese carbonate ore in northern Guizhou: 1. Conduct experiments on the mutual influence of mineral particles and pulses on actual ore, and provide a reference for ore grinding methods, grinding fineness, etc., in order to design the most effective grinding process. Prevent the occurrence of overgrinding and insufficient grinding degree. 2. Conduct magnetic field strength and pulse interaction tests on the ore to provide a reference for magnetic separation conditions, equipment, and processes, in order to prevent fine-grained magnetic minerals from running out, leading to a decrease in recovery and resource waste. 3. Based on the above process research, conduct research on pH adjustment, dosing, and changing grinding methods of the slurry to strengthen magnetic separation experiments, achieve effective magnetic separation and recycling of Qianbei manganese carbonate ore, and provide a theoretical basis for the development of Qianbei manganese ore. The specific test process is as follows.

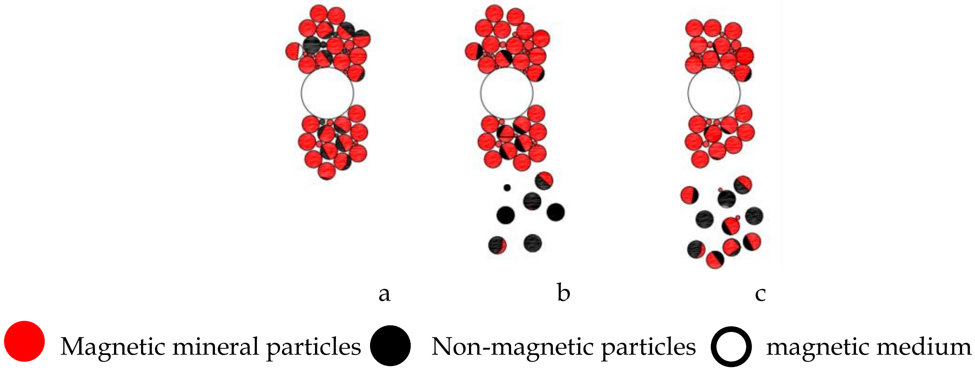

Fig. 13. Actual ore capture of manganese carbonate by high gradient pulse magnetic separator

4.1 Experimental study on the influence of the interaction of magnetic separation factors on rhodochrosite magnetic separation recoveryInteraction test of manganese carbonate mineral particle size and impulse impulse

4.1.1 Test on the mutual influence of particle size and pulse frequency of manganese carbonate minerals

Screen the ore and select several particle size grades of manganese carbonate minerals. After ore blending, ensure that the manganese grade of each particle size grade of the ore is the same. After a magnetic field intensity of 1.2 T and pulse as a variable, the influence of mineral particle size and pulse frequency on the magnetic separation and recovery of manganese carbonate was investigated. The experimental process is shown in Fig. 14.

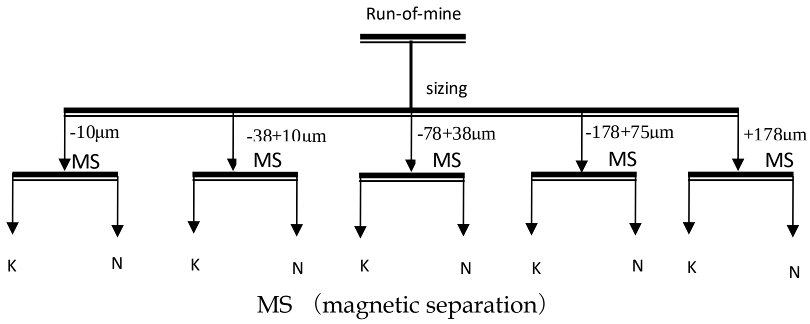

Fig. 14. Test flow

4.1.2. Magnetic field strength and pulse impulse interaction test

Grind and screen the ore, select the appropriate particle size of the ore, and ensure that the mineral particle size composition is the same. The magnetic field strength and pulse impulse are used as variables to investigate the mutual influence of magnetic field strength and pulse impulse on the magnetic separation and recovery of manganese carbonate. The experimental process is shown in Fig. 15.

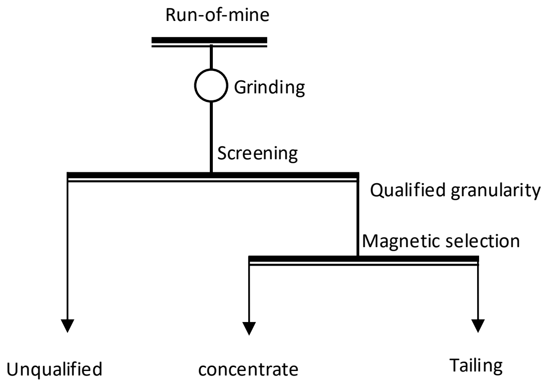

Fig. 15. Test flow

4.1.3. Volume susceptibility and pulse impulse interaction test of manganese carbonate

Conduct grinding operations on the crushed manganese carbonate ore, with a grinding fineness of -200 mesh accounting for 80%. After a rough selection, the magnetic field intensity is 1.2 T, with a pulse of 200 r/min, and the magnetic field intensity is changed to 1.3 T by scanning. Other conditions remain unchanged. Perform AMICS analysis on each product during the secondary selection process, and study the effect of specific magnetization coefficient on the magnetic separation and recovery of manganese carbonate based on mineral maps, recovery of different magnetic particle particles, and recovery of magnetic minerals with different dissociation degrees, The experimental process is shown in Fig. 16.

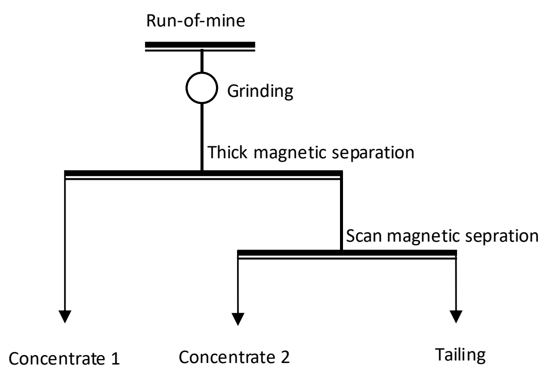

Fig. 16. Test flow

4.1.4. Magnetic separation test for actual pH and dosing system of manganese carbonate ore

The effect of mineral surface potential on the recovery of manganese carbonate was studied based on the pH of the adjusted slurry and the dosing system. The experimental results are shown in Fig. 16.

4.2. Optimization magnetic separation test for actual manganese carbonate ore

Conduct experiments based on the research content, conduct optimal magnetic separation experiments on manganese carbonate, and provide theoretical references for the magnetic separation and recovery of manganese carbonate.

5. Test results and discussion

5.1. Test results

5.1.1. Experimental study on the influence of ore particle size and pulse interaction on the recovery of manganese carbonate

Conduct high-gradient magnetic separation research experiments on the mutual influence of different particle size levels and pulses on the recovery of manganese carbonate ore. Confirming the calculation results to predict mineral particle size and pulse frequency. The calculated value of magnetic field strength selection is 1.2 T, and the test results are shown in Fig. 17.

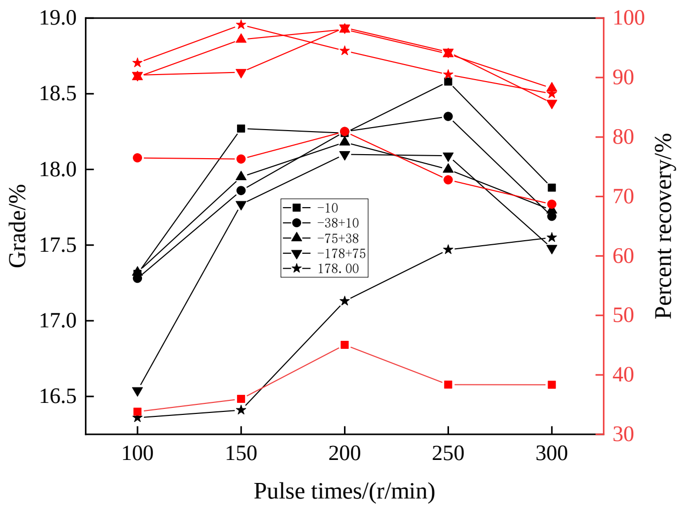

Fig. 17. Effect of manganese carbonate particle size (μm) and pulse interaction on concentrate

As shown in Fig. 17, with the increase of manganese carbonate particles, the manganese recovery also increases, which is consistent with the above calculation results. However, during the process of pulse rate change, the manganese recovery increases first and then decreases with the increase in pulse rate. When the pulse rate increases from 100 r/min to 200 r/min, the manganese recovery increases, but after 200 r/min, the manganese recovery decreases. The recovery does not match the results calculated in Fig. 6 when the recovery continues to increase after 200 r/min. 1. Because the calculation did not take into account the impact of isomorphism, co-association, and dissociation degree of actual ore on the recovery of manganese carbonate. 2. Because the calculation only considers the formation of single-layer magnetic adsorption of manganese carbonate on the surface of the magnetic medium, although manganese carbonate cannot form magnetic chains and beams like magnetite and other strong magnetic minerals in the actual magnetic separation process, it will also form multi-layer magnetic adsorption layers. There is an electric potential difference between manganese carbonate and gangue minerals, forming aggregates that will form magnetic encapsulation during the magnetic separation process. As shown in Figs. 11-12, the calculation results show that multi-layer magnetic adsorption of manganese carbonate is much more difficult than single-layer magnetic adsorption. Therefore, if the pulse duration is too small, the gangue minerals are magnetically encapsulated and the magnetic aggregates formed with manganese carbonate are difficult to disperse. If the pulse duration is too small, it cannot achieve the effect of dispersing and removing gangue minerals, resulting in a decrease in the magnetic medium interaction surface and an incomplete adsorption layer, leading to a decrease in recovery. When the pulse duration is too high, the number of interactions between ore particles and magnetic media increases. However, if the pulse duration is too high, the competitive effect increases, thereby reducing the force of magnetic media on manganese carbonate particles. This causes small particles and partially dissociated particles that can be recovered under smaller pulses to be washed away by water flow, leading to a decrease in recovery. But the optimal conditions for the experimental pulse and the predicted pulse rate of 200 r/min are completely consistent. In the experiment, the actual particle diameter of manganese carbonate ore ranged from 0.074 to 0.038 mm (with a radius of 0.037 to 0.019 mm), and the best comprehensive results were achieved for the recovery and grade of manganese carbonate, which were 98.10% and 18.18%, respectively. Consistent with the predicted particle radius of 0.020 mm as the optimal particle size based on the calculation results.

5.1.2 Experimental study on the influence of the interaction between magnetic field intensity and pulse frequency on the recovery of manganese carbonate

Conduct high-gradient magnetic separation research experiments on the recovery of manganese carbonate ore with different external magnetic field intensities and pulses to study the impact of the interaction between external magnetic field intensities and pulses on the recovery of manganese carbonate, and confirm the predicted external magnetic field intensities and pulses based on the calculation results. To ensure that the calculation results can effectively reference the actual ore sorting, the experiment uses a rod mill to grind manganese carbonate ore and uses screening to remove larger material particles. Magnetic separation tests are conducted on ores with a radius of 0.037-0.019mm and a larger proportion. The test results are shown in Fig. 18.

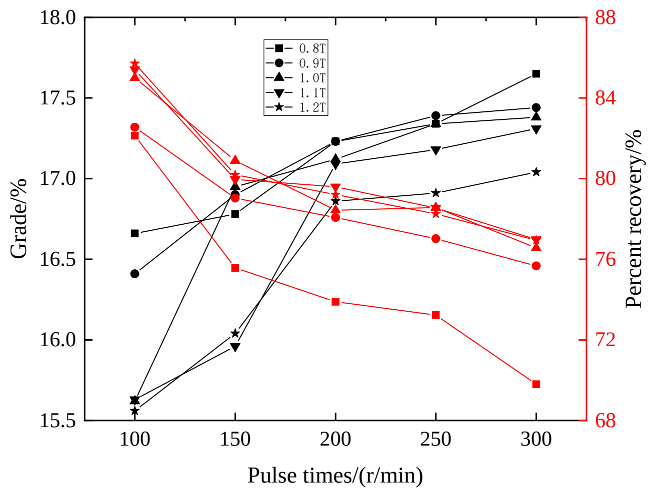

Fig. 18. Influence of magnetic field strength and pulse interaction on concentrate

As shown in Fig. 18, as the external magnetic field intensity increases, the manganese recovery also increases and the grade decreases, which is consistent with the calculation results in Fig. 8. When the pulse rate reaches 200 r/min, the recovery of metal manganese tends to stabilize with the increase in pulse rate, but the recovery still shows a downward trend. The main reason is that increasing the pulse rate reduces the interaction force between manganese carbonate and the magnetic medium. Fine particle manganese carbonate is difficult to magnetically adsorb on the magnetic medium under larger pulse rates, resulting in a decrease in recovery. As the magnetic field intensity increases, the recovery of the concentrate tends to remain unchanged within the error range after reaching 1.0 T, and the predicted magnetic field intensity of 0.9 T in Fig. 8 increases by 0.1 T. 1. The actual manganese carbonate ore is embedded with fine particle size and serious isomorphism, so it is difficult to achieve effective monomer dissociation by using the grinding method. Non-magnetic gangue minerals are associated with manganese carbonate ore, reducing the volume susceptibility of particles. 2. The composition of manganese carbonate ore is complex. calcite, dolomite, clay minerals, and manganese carbonate will form aggregates. The volume susceptibility of aggregates is determined by a variety of minerals, weakening their specific magnetic susceptibility. The calculation results in Fig. 7 show that the volume susceptibility will also affect the recovery of manganese carbonate. When the incomplete dissociation and aggregation are mainly composed of gangue minerals, the surface of the particles is a non-magnetic mineral, and the passage of manganese carbonate particles in the particles results in a decrease in recovery. Therefore, the experimental results are larger than the calculated results. Compared to the experimental results in Fig. 17, the trend of manganese recovery increasing first and then decreasing with the pulse no longer exists. 1. Materials that do not undergo particle size level control will form fine-grained materials that adsorb onto larger particles, and larger particles carry fine-grained materials to overcome competitiveness and fully act on the surface of the magnetic medium. 2. When large particles form a magnetic adsorption layer, their gaps become larger, and fine materials act intermittently, reducing the effect of pulse competitiveness on fine materials.3. From the calculation results in Fig. 6, it can be seen that the recovery is related to the particle size. When fine-grained materials adsorb onto the surface of large-grained materials, the total magnetic field force of fine-grained materials increases due to the influence of large-grained materials.

5.1.3. Test on actual magnetic separation conditions of manganese carbonate ore

Based on the above research, experiments were conducted on the actual ore conditions of manganese carbonate, and the experimental results are shown in Fig. 19.

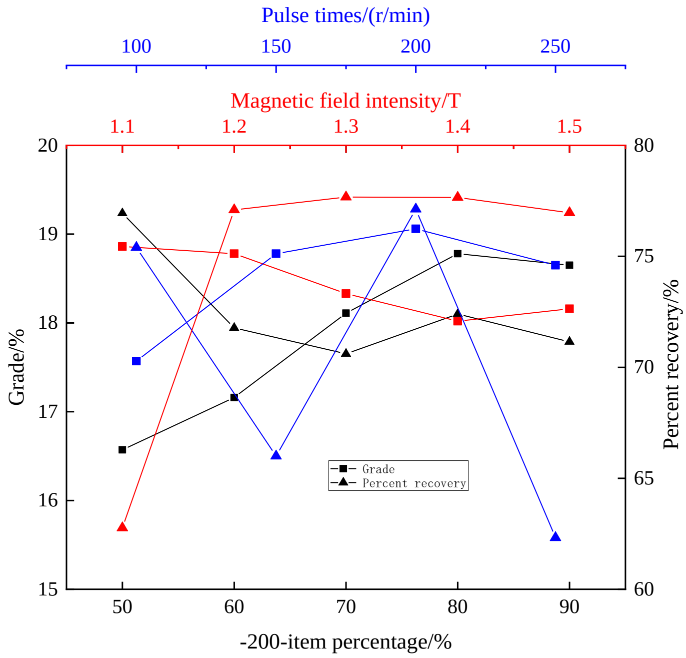

Fig. 19. Magmanganese carbonate

As shown in Fig. 19, after several sets of experimental comparisons, it can be concluded that the optimal experimental conditions for magnetic separation of manganese carbonate ore in northern Guizhou are: ore fineness of -200 mesh accounting for 80%, pulse rate of 200 r/min, and optimal external magnetic field strength of 1.2 T. Under these conditions, the concentrate grade is 19.06%, and the recovery is 76.85%. The optimal magnetic separation tailings selection and scanning magnetic separation test for the above experiment, with an increase in magnetic field intensity of 1.3 T, obtained a magnetic separation index of 18.00% manganese grade in the mixed concentrate and a recovery of 85.86%.

The experimental results show a deviation from the calculated magnetic field strength. Therefore, AMICS analysis was conducted on each product during the magnetic separation process, and the reasons for the deviation between the test results and the calculation results are shown in Fig. 20.
Manganese carbonate ore has a complex composition and fine embedded particle size, which makes it difficult to realize monomer dissociation. Fine gangue minerals are adsorbed on the surface of coarse manganese carbonate ore, and fine gangue minerals form aggregates with fine manganese carbonate ore. These reasons reduce the volume ratio of manganese carbonate particles and the magnetization of particles under the external magnetic field. The external magnetic field strength of the formation test results is greater than the calculated results. As shown in Fig. 20, in concentrate 1, manganese carbonate is mainly present, with complete monomer dissociation and larger particles. Its specific magnetization coefficient is high, and the grade of metallic manganese in the concentrate is relatively high. After increasing the magnetic field intensity to 1.3T, the particles in concentrate 2 are smaller than those in concentrate 1, resulting in a decrease in manganese carbonate content and dissociation degree, a decrease in specific magnetization coefficient, and a decrease in concentrate quality. The tailings are mainly composed of illite and albite gangue minerals, which have low specific magnetization coefficients, making the particles appear as non-magnetic minerals. It is difficult to recover manganese carbonate in the particles, resulting in the tail run of carbonic acid, and the recovery is reduced.

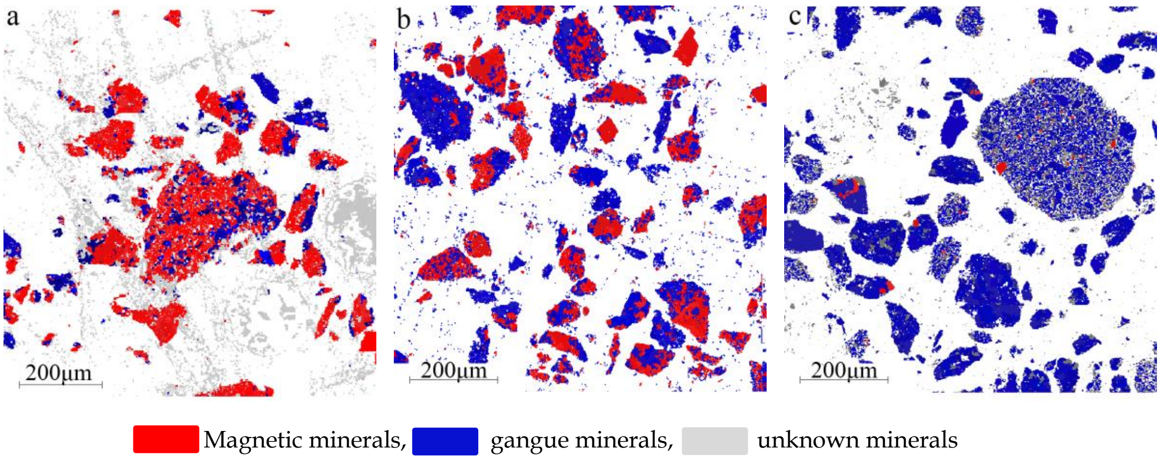

Fig. 20. Plot of carbonate dissociation and recovery status for AMICS analysis, a. concentrate 1. b. concentrate 2. c.tailings

The analysis of the impact of the degree of dissociation of magnetic minerals in each product during the magnetic separation process on the recovery is shown in Fig. 21. From Fig. 21, it can be seen that in various products of magnetic separation, the lower the dissociation degree of magnetic particles, the greater the yield in tailings, and very few particles achieve complete dissociation in each product. 1. Manganese carbonate with fine particle size and difficulty in monomer dissociation. 2. The composition of manganese carbonate ore is complex, and the particles are too fine, which exacerbates the phenomenon of mud formation and agglomeration, leading to the dissociation of individual manganese carbonate particles and the formation of aggregates with gangue minerals. 3. Manganese carbonate has severe isomorphism. The above reasons make it difficult to achieve monomer dissociation of manganese carbonate. The magnetization recovery of weakly magnetic manganese carbonate minerals is related to particle size and composition, with large particles and low dissociation of monomers, and a large proportion of gangue minerals in the ore. Fine particles cause aggregation with gangue minerals. These reasons result in a decrease in the specific magnetization coefficient, making it difficult to recover.

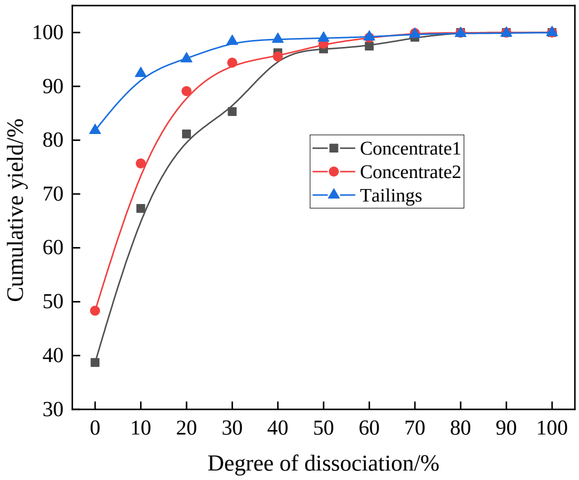

Fig. 21. Recovery diagram of different manganese carbonate dissociation degrees in the product

The analysis of the impact of the size of magnetic mineral particles in each product during the magnetic separation process on the recovery is shown in Fig. 22. As shown in Fig. 22 when the mineral particles are greater than 31.53 μm. It is mostly presented as concentrate 1, which accounts for a small proportion of tailings and concentrate 2. The proportion of small particles in concentrate 1 and concentrate 2 is small, and the intermediate particles that are difficult to recover in the rough selection are mostly due to small particle dissociation and particle size, low specific magnetization coefficient, and low magnetic force to mineral particles. It is difficult to recover at 1.2 T, but increasing to 1.3 T increases the magnetic force of the magnetic medium, which in turn reduces competitiveness and increases the recovery of manganese, resulting in a decrease in concentrate quality.

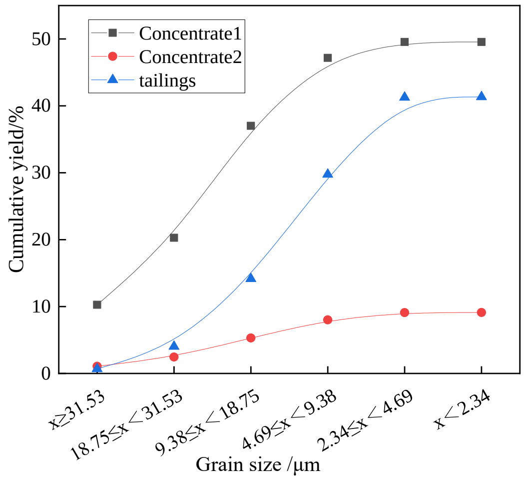

Fig. 22. Recovery diagram of different carbonate particle sizes in the product

5.1.4. Experimental study on optimizing magnetic separation of manganese carbonate ore

Magnetic separation experiments were conducted using 5.1.2 medium grinding fineness of -200 mesh 80%, pulse rate of 200 r/min, coarse magnetic separation of 1.2 T, and scanning magnetic separation of 1.3 T as the basic data. The following optimization experiments were conducted separately. Firstly, adjust the pH of the ore slurry, change the surface potential of the mineral to cause homogeneous agglomeration of fine manganese carbonate, change the size of magnetic particles, reduce the phenomenon of fine particle tailing, and increase the concentrate recovery. Secondly, by adding flocculants, mineral flocculation can increase the size of mineral particles, reduce the phenomenon of fine particle tailing, and increase the recovery of manganese carbonate. Thirdly, by pre-screening and grinding, the occurrence of overgrinding of fine mineral particles in the raw ore can be prevented. Fourthly, by pre-checking the screening and grinding method, it is necessary to prevent the occurrence of sliming and overgrinding of fine-grained minerals in the raw ore and minerals that first reach the beneficiation particle size during the grinding process. The conditions for each group of magnetic separation tests are a rough magnetic field strength of 1.2 T, a scanning magnetic field strength of 1.3 T, and a pulse rate of 200 r/min. The test results are shown in Fig. 23.

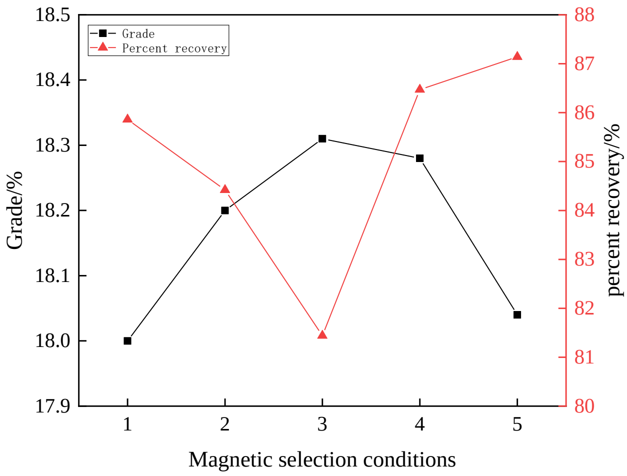

Fig. 23. Recovery of manganese carbonate under different conditions. 1. Convention, 2. sodium carbonate 8 kg/Mg, 1. sodium polyacrylate 400 g/Mg, 4. prescreening, 5. Pre-check the screening score

As shown in Fig. 23, without the addition of reagents, the grinding fineness of -200 mesh is 80%. After one coarse and one sweep magnetic separation test, the mixed concentrate manganese grade is 18.00%, and the recovery is 85.86%. By adding sodium carbonate to adjust the pH of the slurry to 10, the surface potential of manganese carbonate ore was in a low potential state. A one coarse one sweep magnetic separation experiment was conducted on it, and the manganese grade of the mixed concentrate increased by 0.20%, while the recovery decreased by 1.44%. According to the AMICS analysis of each product in 5.1.3, it can be concluded that manganese carbonate particles that can achieve complete dissociation do not exist in each product, and there are gangue minerals present in each particle. After adjusting the pH of the slurry, the surface potential values between other minerals are relatively high, and flocculation will not occur, resulting in the aggregation of encapsulated manganese carbonate particles and smaller exposed manganese carbonate particles. Small and incompletely dissociated manganese carbonate particles are difficult to capture and be taken away by water flow, reducing their recovery and increasing the quality of the concentrate. Choosing to use pH adjustment as the flocculation pathway to meet the high requirements for mineral dissociation, for magnetic separation and recovery of fine-grained materials, adjusting the pH value of the slurry for flocculation and recovery can be chosen. Adding sodium polyacrylate flocculant to the slurry to flocculate fine manganese carbonate materials resulted in a 0.31% increase in mixed concentrate grade and a 4.42% decrease in recovery. Sodium polyacrylate has low flocculation selectivity. When tap water is used as a slurry carrier, sodium polyacrylate has a flocculation effect on all fine-grained minerals. The presence of each component in the aggregate reduces its volume magnetization, making it difficult to recover and causing the loss of recoverable manganese carbonate particles, resulting in a decrease in recovery. The flocculation and recovery of sodium polyacrylate should regulate the pH value of the slurry, to have certain selectivity under low addition conditions. Conduct pre-screening and grinding tests, and mix the ground ore with the materials under the screen evenly. The required grinding fineness of -200 mesh is 80%. Conduct magnetic separation tests, and the manganese grade of the mixed concentrate has increased by 0.28%, and the recovery has increased by 0.61%. According to the calculation results in Fig. 6 and the experimental results in Fig. 17, the optimal particle diameter of manganese carbonate particles is 0.074-0.038 mm. Pre-screening of materials smaller than 0.074 mm can ensure the proportion of materials at this particle size level and effectively reduce the overgrinding of ore that reaches monomer dissociation in the raw ore, thereby suppressing agglomeration. After pre-screening -200 mesh materials, it can effectively improve the concentrate grade and recovery. Pre-inspection and screening tests were conducted on the ore samples, and all samples were subjected to mixed magnetic separation. The mixed concentrate grade was increased to 0.04%, and the recovery was increased by 1.28%. Pre-inspection and screening not only have the function of pre-screening but also crush the materials that reach the separation particle size level during the grinding process. Compared to pre-screening, it can better ensure the proportion of 0.074-0.038 mm particle size and effectively improve the recovery of manganese carbonate.

5.1.5. Effect of mineral composition of manganese carbonate particles on magnetic separation

The effect of calcium manganese homogeneous phase on the high gradient pulse magnetic separation recovery of manganese carbonate ore

The manganese lattice in manganese carbonate ore is often replaced by calcium, magnesium, iron, etc., forming isomorphism. The changes in the content of calcium, magnesium, and iron in the ore have a significant impact on the magnetic separation of the ore. The increase in iron content in the lattice can cause an increase in mineral magnetism, which is beneficial for mineral magnetic separation. The increase in calcium and magnesium content is unfavorable for magnetic separation. Perform all spin polarization density functional theory (DFT) calculations using the Perdew Burke Ernzerhof (PBE)(Kresse et al., 1996) formula in generalized gradient approximation (GGA) using first principles (Kresse et al., 1996; Kresse et al., 1999). The projection augmented wave (PAW) potential (Perdew et al., 1996; Blöchl et al., 1996) is selected to describe the ion nucleus, and the plane wave basis set with kinetic energy cut-off value of 400 ev is used to consider valence electron. The use of the Gaussian smear method and a width of 0.05 eV allows for the partial occupation of the Kohn Sham orbit. Geometric optimization is considered convergent. According to the following five configurations, calculate the magnetic moments of each atom of manganese carbonate ore with calcium-like substance in different configurations. Compare the magnetic moment differences of each configuration to study the effect of Ca-doped manganese carbonate on the magnetic moment of manganese carbonate. The calculation results are shown in Fig. 25. (The serial number in Fig. 25 represents the calculated magnetic moment of each atom in the configuration).

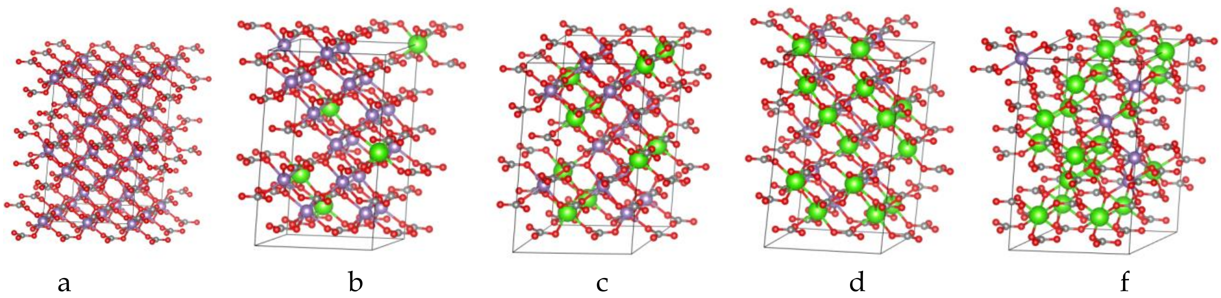

Fig. 24. The Ca-doped manganese carbonate configuration was calculated by VESTA a: manganese carbonate b: 20% calcium-doped manganese carbonate c: 40% calcium doped, manganese carbonate d: 60% calcium-doped manganese carbonate f: 80% calcium-doped manganese carbonate

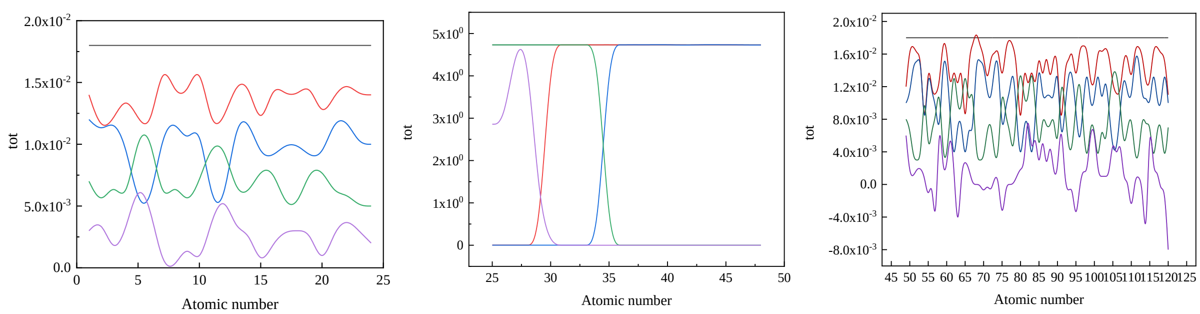

Fig. 25. Results of the magnetic moment of Ca doping by VESTA

As shown in Fig. 25, for systems with different doping of $MnCO_3$, the lattice constants of the two types of magnetism vary, and from an energy perspective, the antiferromagnetic ability is lower. Ca doping with manganese carbonate affects the atomic magnetic moment. As the doping amount increases, the magnetic moment of manganese carbonate decreases. When the Ca doping amount reaches 80%, the atomic magnetic moment shows a negative value, resulting in a total magnetic moment decrease of 16.31 points in this configuration, which is 98.977 points lower than the undoped configuration of manganese carbonate. This causes the transformation of calcium manganese ore into manganese calcite, resulting in a low specific magnetization coefficient for calcium-type minerals, making it difficult to recover these minerals through magnetic separation. Therefore, the magnetic elements in non-magnetic elements and homogeneous magnetic minerals cause a decrease in the magnetic moment of magnetic minerals, resulting in a lower specific magnetization coefficient and breaking away from the boundaries of magnetic minerals, making it difficult to recover through magnetic separation.

The effect of intergrowth on high gradient pulse magnetic separation of manganese carbonate ore intergrowth is inevitable in actual ores. In crushing and grinding operations, ores do not always fracture along mineral boundaries, resulting in the presence of intergrowth in minerals. Manganese carbonate magnetic separation is based on the difference in its specific magnetization coefficient and gangue minerals. When the content of gangue minerals in the intergrowth is too high, the particle-specific magnetization coefficient is small and difficult to separate. Compared to the influence of Mn on the specific magnetization coefficient of manganese carbonate mineral particles in elements such as Ca, the influence of intergrowth on the specific magnetization coefficient of manganese carbonate mineral particles is more intuitive. The formula for calculating the volume-specific magnetization coefficient of connected body manganese carbonate particles is shown in Eq. 8 (Wang et al., 2022).

$$X_{连} = \frac{\gamma_1 X_1 + \gamma_2 X_2 + \cdots + \gamma_i X_i}{\gamma_1 + \gamma_2 + \cdots \gamma_i} \tag{8}$$

Assume that the volume susceptibility of manganese carbonate is $X = 200 \times 10^{-6}\ cm^3/g$, calcite volume susceptibility $X_1 = 2.2 \times 10^{-9}\ cm^3/g$, calculate the volume susceptibility of manganese carbonate and calcite intergrowth with different contents. The calculation results are shown in Fig. 26.

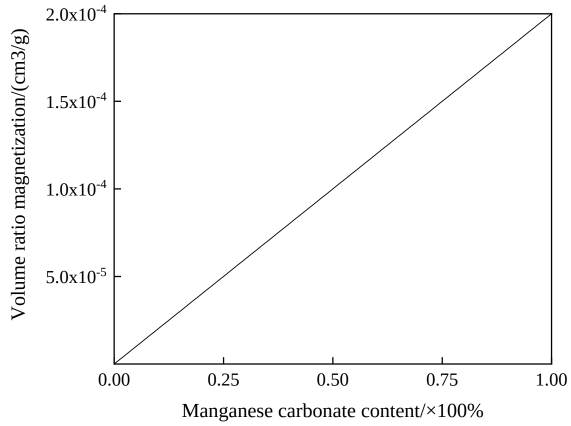

Fig. 15. Volume ratio susceptibility of different contents of manganese carbonate and calcite complexes

From Fig. 26, it can be seen that the influence of manganese carbonate content on the volume-specific magnetic susceptibility of connected particles is directly proportional, while the influence of non-magnetic mineral calcite content on the volume-specific magnetic susceptibility of connected particles is inversely proportional. As the content of calcite in connected particles increases, the volume-specific magnetic susceptibility of connected particles decreases linearly with a slope of -0.0001999978.

Calculation of the capture yield p of manganese carbonate granular isomorphs and associated organisms

The formula for calculating the isomorphism and association of manganese carbonate particles is as follows:

$$P = K\frac{F_m}{F_C} = K\frac{\beta F_m}{F_C}$$

where β is the proportional constant.

When gangue minerals belong to weakly magnetic minerals, the specific magnetic susceptibility of gangue minerals is much smaller than that of manganese carbonate, and can be ignored. The calculation of the collection probability of connected bodies can be abbreviated as the following equation.

$$P = K\frac{F_m}{F_C} = K\frac{\gamma F_m}{F_C}$$

Compared to manganese carbonate particles of the same volume, the capture rate of the connected bodies is higher than that of manganese carbonate particles γ In addition, the gangue minerals formed in intergrowth with manganese carbonate ore are mainly calcite and Baiyunshan. When the content of gangue minerals is too high, the particles generally enter the ranks of non-magnetic particles, resulting in being carried into the tailings by water flow during the high gradient pulse magnetic separation process, reducing the recovery of manganese carbonate.

5.2. Discussion

The probability of using a single-layer magnetic medium with a high gradient pulse magnetic separator to capture manganese carbonate particles is used to predict the actual conditions for magnetic separation of manganese carbonate ore. The predicted particle size and pulse frequency are fully consistent with the optimal conditions for actual ore magnetic separation. The actual magnetic field intensity of ore sorting is higher than the calculated value, mainly because the actual ore composition is complex, the embedded particle size is fine, and the similarity between minerals is severe, resulting in difficult dissociation of mineral monomers and severe aggregation of fine particles. The selection of calculation results to predict the actual conditions of magnetic separation and recovery of ore must consider the influence of these factors. For manganese carbonate ore with severe isomorphism, a coefficient that affects the volume magnetization needs to be added for calculation, and the proportion coefficient of manganese carbonate ore needs to be added for the calculation to predict the actual magnetic separation recovery conditions of the ore, which can make the conditions more accurate. The formation of a multi-layer magnetic adsorption layer through magnetic separation recovery must consider the influence of slurry pH value, and the electrostatic force between multi-layer magnetic adsorption particles has a significant impact on it. The influencing factors of magnetic separation of manganese carbonate ore are not only related to mineral particle size, external magnetic field conditions, and pulse competitiveness, but also related to ore isomorphism, co-association relationship, embedded particle size, and constituent minerals. After determining the research of mineralogy of the manganese carbonate ore process, it is completely possible to predict the actual conditions of magnetic separation recovery of manganese carbonate ore through calculation, provide a theoretical basis for the actual magnetic separation recovery of manganese carbonate ore, and reduce the consumption of resources and manpower.

6. Conclusions

In the process of high gradient pulse magnetic separation, the single-layer magnetic medium capture rate of manganese carbonate increases with the increase of mineral particles; It increases with the increase of volume susceptibility of manganese carbonate; Increasing with the increase of external magnetic field intensity; It decreases as the number of pulse impulses increases.

In the process of the high gradient pulse magnetic separation of manganese carbonate, multi-layer magnetic adsorption in magnetic media is more difficult than single-layer magnetic adsorption. There is an electrostatic force between multi-layer magnetic adsorption mineral particles, and the electrostatic force between clusters of manganese carbonate minerals is repulsive. The existence of electrostatic force increases competitiveness, leading to a decrease in capture efficiency and affecting the formation of multi-layer magnetic adsorption in magnetic media.

The calculation of the single-layer capture rate of manganese carbonate and the probability of multi-layer magnetic adsorption can effectively predict the actual magnetic separation conditions of the ore. There may be deviations in the magnetic field strength, and the influence of isomorphism, connected bodies, and aggregates needs to be considered. The influence coefficient needs to be added to the calculation.

After calculation results and actual ore magnetic separation experiments, the optimal conditions for magnetic separation of manganese carbonate ore were determined to be grinding fineness of -200 mesh 80%, magnetic field strength of 1.2 T, and pulse rate of 200 r/min. Under these conditions, a manganese concentrate grade of 19.06% was obtained with a recovery of 76.85%.

Adjusting the pH of the slurry and adding flocculants to optimize the magnetic separation and recovery of manganese carbonate is difficult to improve under a single condition. Pre-screening and pre-inspection screening can effectively reduce the aggravation of the mineral mud agglomeration phenomenon. After optimizing the conditions, the optimal data obtained is the manganese concentrate grade of 18.04% and the recovery of 87.14%.

Acknowledgments

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