A geometallurgical approach to enhance the gravity beneficiation of a strontium deposit

A. Perroton[1], T. Wallmach[1], S.B. Blancher[1], and G. Rameau[1]

Affiliation:
[1]Eramet Ideas, Trappes, France.

Correspondence to:
A. Perroton

Email:
arthur.perroton@eramet.com

Synopsis

Mineralogical analyses and QEMSCAN® process simulation were used to characterize a heavy mineral concentrate of celestine originating from the Beni Mansour deposit in Algeria, and to model a gravity separation process to remove Sr-, Ba-, and Ca-bearing impurity phases. By analysing the partitioning of Ba, it was shown that the very small amounts of barite present in the sample could not account for the chemically derived Ba concentration in the total sample. It was therefore decided to investigate the presence of Ba that could replace the Sr in celestine in the form of solid solution substitution. It was found that some celestine particles displayed zonation textures with respect to Ba, resulting in difficulties in meaningfully reducing the Ba content without a significant loss of Sr. It was shown that the removal of all barite would lead to a minimum of 0.65 wt% Ba in the final celestine concentrate. Density separation modelling by QEMSCAN® software showed that the 3.5–4.0 g/cm^3 density fraction had higher Sr and celestine concentrations, as high as 46.33 wt% Sr. In this particular fraction, the Ba and Ca contents could be reduced to 0.72 wt% and 0.49 wt% respectively.

Keywords

process mineralogy, geometallurgy, modelling, density separation, QEMSCAN®.

Introduction

Chemical surveys performed on Beni Mansour deposit in the past for resource estimation did not include detailed mineralogical information and interpretation. By including this information, it is possible to predict the process behaviour of minerals in a way that can make the difference between a mineral resource of potential economic interest and a mineral reserve of definite economic value. Mine planning is increasingly performed based on mineralogical and process-related factors that can be simulated with the QEMSCAN® software. The literature provides numerous examples of applications and case studies to indicate how automated mineralogy can add value to process improvement. Within the past few years a large number of papers and communications have been published on the interactions of automated mineralogy, ore processing, and geometallurgy (Lotter *et al.*, 2011; Schouwstra and Smit, 2011; Baum, 2014; Gu, Schouwstra, and Rule, 2014; Zhou and Gu, 2016; Becker, Wightman, and Evans, 2016; Delaporte *et al.*, 2018, 2019).

Study aims

The sample was provided by an Eramet Ideas external customer in order to demonstrate the QEMSCAN® application for mineral characterization and to provide process-related information.

The celestine concentrate was analysed with respect to its chemical and mineralogical composition. The objectives of these analyses were to:

➤ Identify the minerals present in the sample
➤ Identify mineral impurities, particularly those containing Ca and Ba
➤ Propose physical methods to improve the quality of the Sr concentrate.

The provided sample had a high Sr concentration of 46 wt%. This corresponds with the very high content of celestine, amounting to 97 wt%. The barium content amounted to 0.78 wt%, and calcium to 0.90 wt%. These impurities should be reduced as much as possible to meet the tight specifications of the chemical industry. As the client is currently in a qualification process for its product, the authors were asked to determine the minimum concentrations of Ba and Ca that could be reached in the concentrate by using physical beneficiation techniques.

A geometallurgical approach to enhance the gravity beneficiation of a strontium deposit

This paper aims to show how mineralogical information can aid in making mineral processing decisions, and how SEM/ QEMSCAN® analyses can be used to identify and quantify trace elements that affect the ore quality.

Geological context and identification of the sample

The sample originated from the Beni Mansour deposit in Wilaya de Béjaia, 170 km southeast of Algiers (Algeria). This Triassic complex hosts an important occurrence of celestine mineralization. The mineralization occurs within an elongated Triassic structure trending N80°E, deep-seated in Albian and Cenomanian formations. This Trias consists of monogenic and polygenic breccias cemented by celestine and characterized by various authigenic minerals and several generations of calcite (Moulla and Thibieroz, 1995).

The mine is owned and operated by TBRHO, part of the Zergoun Brothers Group. A 500 g sample of a heavy mineral concentrate, generated by reference shaking table tests, was submitted and studied. Prior to the shaking table tests, the sample was subjected to a three-stage crushing process to reduce the particle size to below 5 mm (TBRHO internal report, 2014). The heavy mineral concentrate was split in two twin samples, one for chemical analyses and one for the mineralogical study

For microscopic observations, in order to obtain a homogeneous and representative polished section, the sample was embedded in liquid epoxy resin. After polymerizing, the resin-mineral mixture was cut perpendicular to its surface, then re-embedded, polished, and carbon coated. This method allows representative analyses of the sample even if particle segregation occurred after placing the sample material into the epoxy resin.

Experimental and analytical methods

The mineralogical characterization was performed using QEMSCAN®, scanning electron microscopy, and electron microprobe analyses. QEMSCAN® is an automated technique for the detailed and statistically significant characterization of mineral and noncrystalline phases, using polished sections, by means of scanning electron microscopy (SEM) coupled with chemical microanalyses by energy-dispersive spectrometry

(EDS). Characteristic EDS spectra generated by the electron beam impinging on the sample are used for the characterization of minerals and phases. The characterization addresses physical, chemical, and textural properties of minerals and phases in order to statistically evaluate this information, individually or in combinations of individual grains or particles (Gottlieb *et al.*, 2000). QEMSCAN® analyses for this project were carried out at the Eramet Ideas Geometallurgy Department using a FEI Quanta 650F SEM platform fitted with two Bruker Xflash 30 mm silicon drift energy-dispersive detectors.

For QEMSCAN® analyses, the sample was divided into six twin fractions, each of which was analysed separately to confirm the representativeness of analyses. Analyses were performed using 2 μm steps to obtain 21 million EDX analyses for classification and grouping, with respect to corresponding minerals or mineral groups that constituted the building blocks of a mineralogical database that served as the basis for QEMSCAN® data treatment and interpretation. The creation of a reliable species identification protocol (SIP) for an ore deposit, which is a mineralogical database, is one of the most critical requirements for precise analyses of any sample. Chemical and physical properties of minerals, such as densities, can be treated with high statistical significance, as discussed in the following sections. A total of 5500 particles were analysed during 46 hours with a working distance of 13 mm and a spot size of 1.2 nm. The results presented in the paper represent the aggregate of these 5500 particles.

The development of a quantitative database needs to be addressed briefly as a rarely applied methodology for QEMSCAN® analyses was used in this investigation. Each SIP entry is based on EDX images generated from photon counts in the SEM detectors. These analyses can be grouped into compositional classes. An example is presented in Figure 1. The counts for Sr, Ba, S, and oxygen for a celestine analysis are presented in this figure (red spectrum). These counts do not directly refer to weight percentages as oxygen is very frequently underrepresented in EDX analyses. Additionally, matrix effects of minerals involving light and heavy elements play a role in the liberation of photons during analysis. The black EDX spectrum in Figure 1 represents
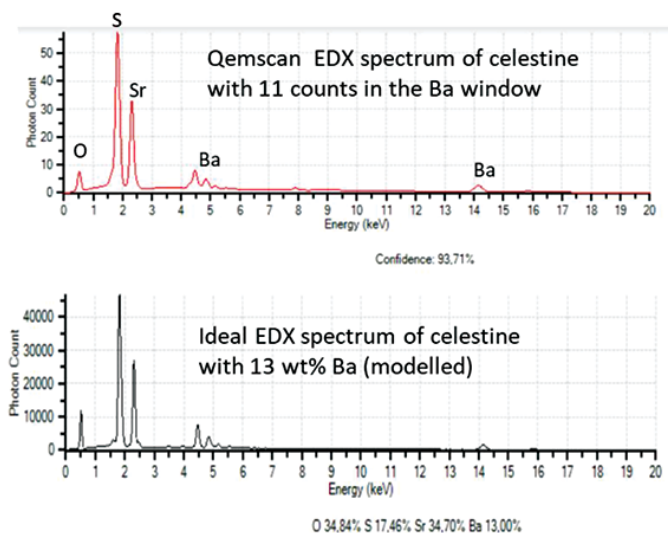
	counts	SIP definition
Sr	49,79	Must Have(In Range: 45.0 - infinity)
Ba	11,77	Must Have(In Range: 11.0 - 12.0)
S	17,95	Must Have(In Range: 10.000 - infinity)
O	6,54	Any amount

Modelled concentrations

Used Elements	
Element	Weight Percentage
O	34,841
S	17,457
Sr	34,702
Ba	13

Figure 1—Comparison of QEMSCAN®-generated EDX spectrum (red) with a modelled ideal EDX spectrum of celestine containing 13 wt% Ba

ideal celestine with precise quantities of elements in weight percentages. The amount of Ba in celestine can be quantified by adding Ba replacing Sr into the simulation software in order to attain an EDX pattern that corresponds to the actual QEMSCAN® analysis. In the case presented in Figure 1, 13 wt% of Sr has been replaced by Ba, resulting in a close match of the QEMSCAN®-generated EDX pattern for this analytical point. It can also be shown that 11.7 photon counts represent 13 wt% Ba in this analysis. In this way, photon counts of Ba in a celestine matrix were converted into weight percentages in the range of 0–10 wt% Ba in celestine. The Ba photon counts are therefore underrepresented in QEMSCAN® analyses, whereas Sr is overrepresented. This is due to the fact the heavier Ba (elemental mass 137.33) is less susceptible for the liberation of photons during QEMSCAN® analyses than lighter Sr (elemental mass 87.62). As mentioned above, the deficiency in oxygen in SEM analyses must also be considered. For precise Sr concentrations in this analysis, a conversion from photon counts into weight percentages is also required. Obtained weight percentages of refined elemental compositions of Ba-bearing celestine were used in the textural interpretations presented in this paper.

Chemistries and densities of the individual phases are entered into the so-called primary list in order to convert area percentages from the image information into weight percentages. The quality of the database can be shown by the very low amount of unidentified minerals (<0.05 wt% 'others') and by comparing the bulk chemical analyses of the sample (XRF) with the recalculated chemistry based on the mineralogical composition. A good correlation ($R^2 > 0.95$) is presented in Figure 2.

Identification of impurities

Barium and calcium deportment

One of the original aims was to trace Ca- and Ba-bearing minerals in the sample. The very small amounts of calcite, dolomite, and barite in the sample (Figure 2) cannot account for the chemically derived concentrations in the analysed sample. It was therefore decided to investigate the possibility of Ba and Ca replacing the Sr in celestine in the form of solid solutions.

The partitioning of Ba and Ca is shown in Figure 3. The X-axes represent QEMSCAN® inferred concentrations of barium (0.8 wt%) and calcium (0.9 wt%). These elements are hosted by various minerals that are represented in different colours. Barium is 85% hosted by celestine (green), replacing Sr in its mineral lattice (Figure 3A). Calcite (cream) and dolomite (blue) host only half the Ca present in the sample (Figure 3B). The remainder of Ca is hosted by celestine, where it replaces some of the Sr. The
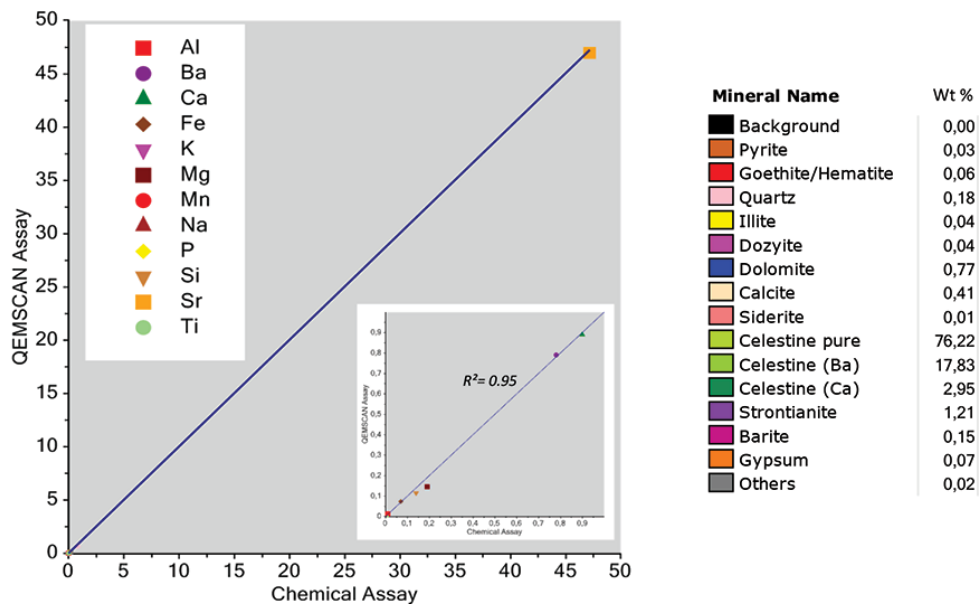

Figure 2—Chemical assay reconciliation with QEMSCAN® recalculated element concentrations. A good correlation ($R^2 > 0.95$) is necessary to confirm a good mineral identification. The mineralogical composition of the investigated sample (in wt%) is presented on the right hand side of the figure
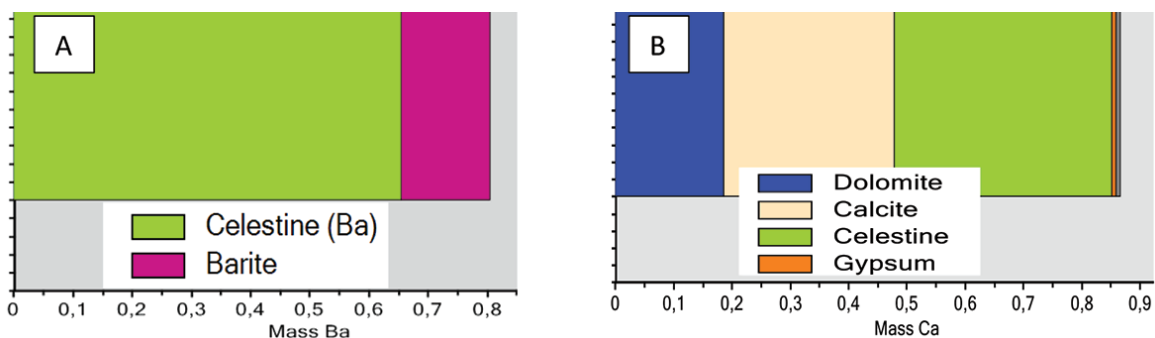

Figure 3—Partitioning of Ba and Ca. The majority of Ba is replacing Sr in celestine (A). Calcium is partitioned equally in CaMg carbonates (calcite and dolomite) and celestine (B)

celestine mineral phase is therefore a solid solution between three end-members: $SrSO_4$ (celestine ss), $BaSO_4$ (barite), and $CaSO_4$ (anhydrite). These two figures show that without any loss of celestine, barite, calcite, and dolomite can be further removed to attain concentrations of 0.65 wt% Ba and 0.37 wt% Ca.

Ba-celestine and Ca-celestine analyses

Celestine particles display Ba-rich zonation textures. Calcium occurs more randomly in small amounts within celestine, but is concentrated in Ba-free parts. Some celestine particles display quasi-rhythmic zonation and the Ba contents can reach several wt% (up to 4 wt%) in distinct zones (Figures 4 and 5).

Association and liberation considerations

Barite, dolomite, and calcite were identified and are present either as liberated minerals or as inclusions in celestine. Some selected QEMSCAN® particle views showing the textural relationships of these minerals with celestine are presented in Figure 6.

The textural relationships presented in Figure 6 can be quantified. Figure 7 presents an association diagram that shows the 'coexistence' (inclusions or attachment to adjacent phases) and the purity of the individual particles. The X-axis presents the analysed minerals; the Y-axis shows the percentage association of each mineral with the same mineral, indicating its purity in particles where it is present, and with other minerals. Celestine is almost completely free of inclusions of other phases. Pure celestine is associated with up to 10% Ba-bearing celestine and up to 2% with Ca-bearing celestine. Barite is associated with up to 30% celestine. Calcite is 70% pure and associated with only small amounts of celestine and strontianite, together totalling 20%.

The association diagram presented in Figure 8 represents interfaces of minerals and the interface of the mineral with the background (free surface). In this approach the purity of a mineral is not displayed. Instead, the diagram presents a quantification of mineral interfaces between texturally associated minerals. The association with the background (free surface, represented by the black portion of each column) carries important information for mineral processing. Should, for instance, calcite or dolomite be removed by flotation or acid leaching, it would be necessary for these minerals to be well liberated with a high percentage of free surface area. In the case of the analysed sample, dolomite and calcite are not very well liberated and show free surfaces of only 8% for calcite and 15% for dolomite. Even if the two minerals are grouped together
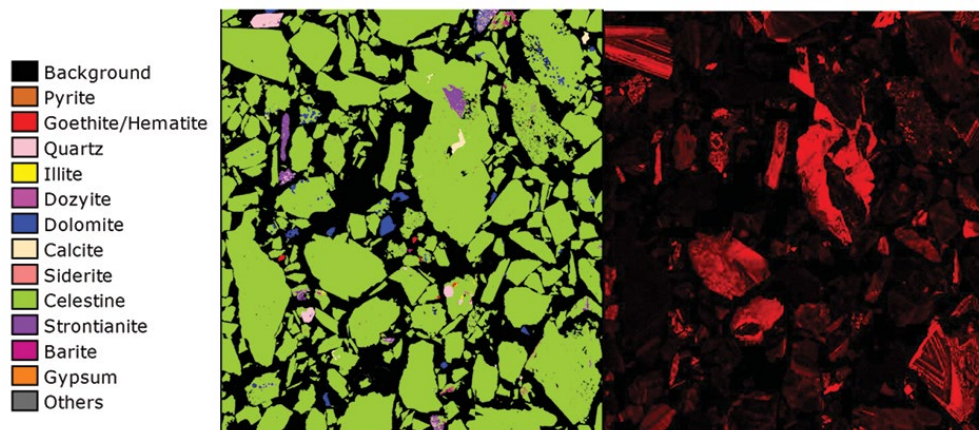

Figure 4—The QEMSCAN® image on the right shows those microanalyses that contain minor amounts of barium (red). Barium is zoned in some particles (bottom right and top left corners)
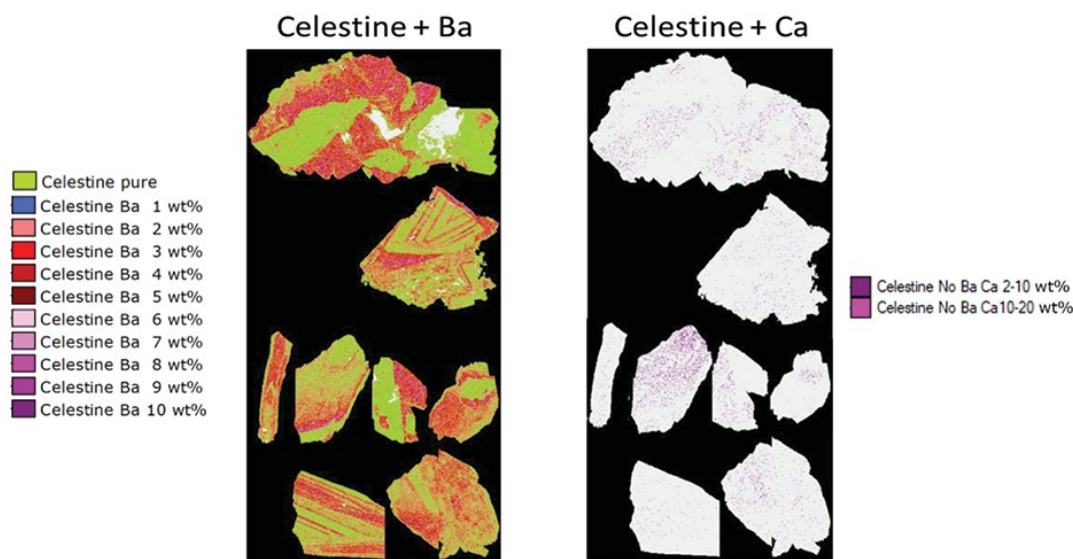

Figure 5—Ba and Ca distribution in celestine particles. Left: celestine particles with highlighted Ba zonation patterns. Right: Ca distribution in celestine particles

A geometallurgical approach to enhance the gravity beneficiation of a strontium deposit
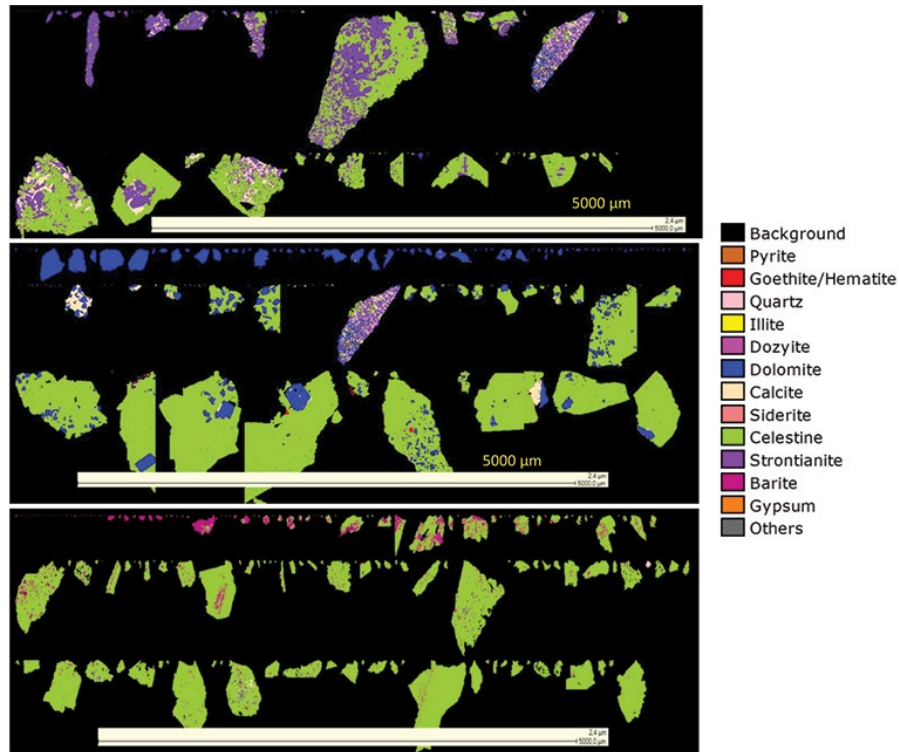

Figure 6—Selected QEMSCAN® views of celestine particles (green) that host strontianite (purple, at the top), dolomite (blue, in the middle), calcite (cre...
middle), and barite (pink, at the bottom). These minerals are either well liberated or occur as inclusions in celestine
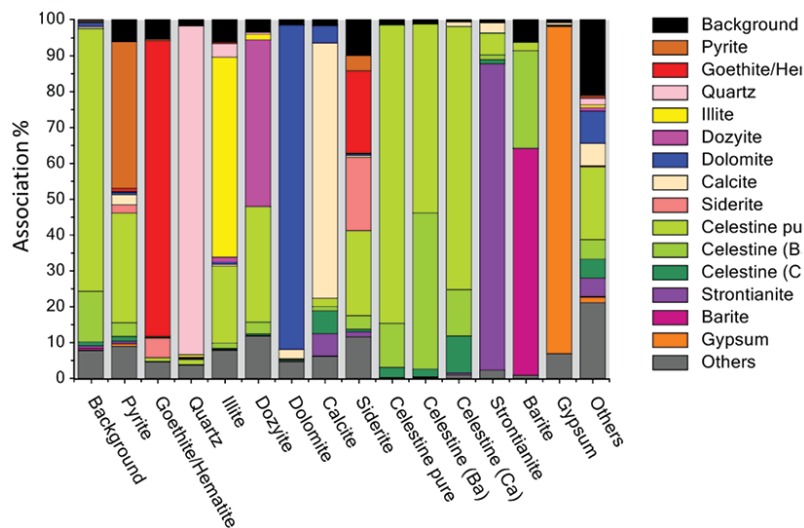

Figure 7—Mineral association diagram normalized to 100% for each mineral. The X-axis represents the identified minerals, each of which is normalized to 100%.
The Y-axis shows the association percentage of each mineral with other minerals that occur as inclusions or adjacent (touching) mineral grains

the free surface will not exceed 20%. The majority of these two minerals are locked as inclusions in other minerals, and therefore they are not good candidates for physical separation methods.

Barite appears to be largely texturally associated with celestine, which again indicates that it will be difficult to significantly reduce the Ba levels in the concentrate. Dolomite and calcite are less frequently associated with celestine and thereby have a greater potential for being removed from the concentrate.

Celestine displays 80% free surface and is by far the best liberated mineral in the sample, indicating a good potential for physical separation methods to be employed in the beneficiation process.

Process modelling as a first indicator to increase the economic quality of samples

The QEMSCAN® software offers a number of process modelling options. The modelling of density separation of particles is of particular interest for this geometallurgical application. Each particle can contain several phases or grains of different densities, chemical compositions, and sizes. The sum of all these variables is taken into consideration in the modelling software.

Density modelling indicates that there is still potential to improve the quality of celestine concentrates. As the analysed concentrate already has a very high content of Sr (45.57 wt%)
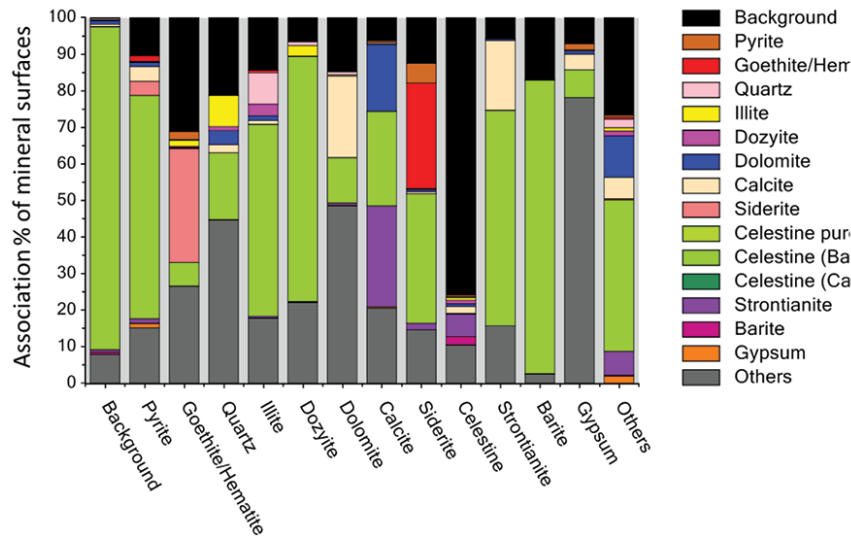
Figure 8—Mineral association diagram displaying the mineral interface percentages (normalized to 100%). Celestine, with 80% association (black portion of the celestine column), is the best liberated mineral in the analysed sample. Calcite and dolomite are not well liberated in terms of free surface, and occur mainly locked in other minerals
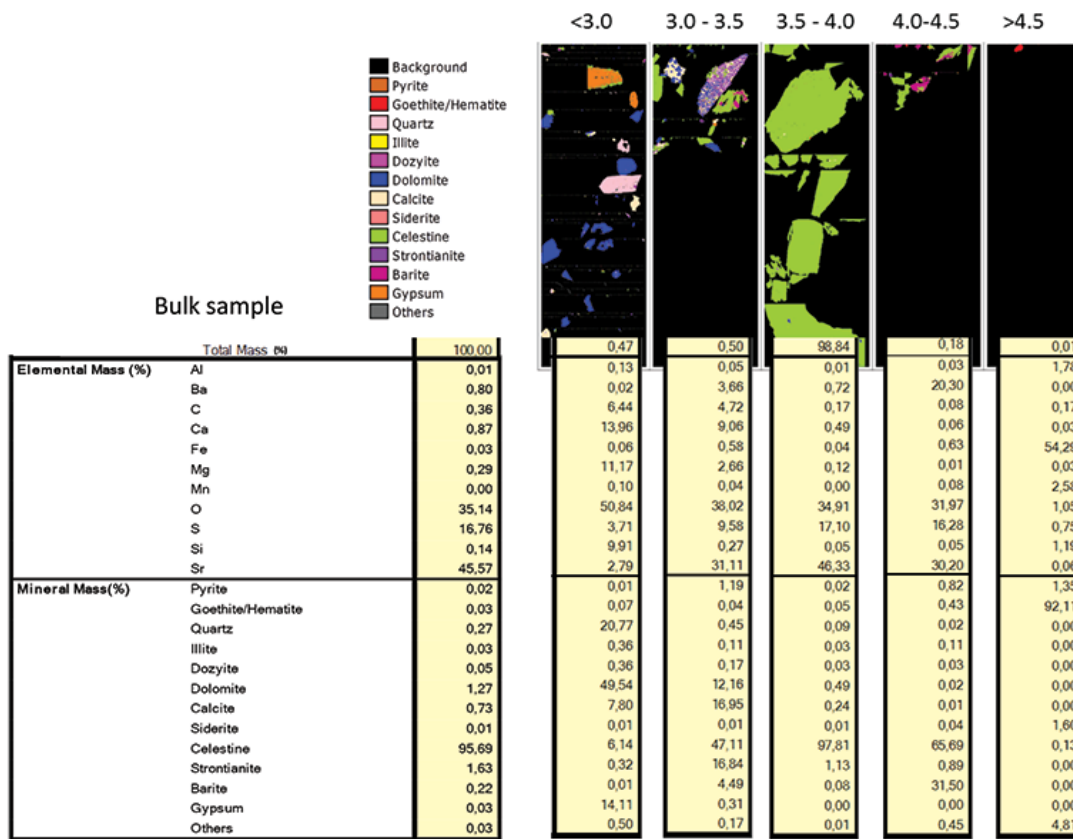

Figure 9—Density separation modelling using density steps of 0.5 g/cm³, from < 3.0 g/cm³ to > 4.5 g/cm³. Each fraction can be represented in terms of chemistry and mineralogy. The mass percentage of each fraction is also indicated on the top of each density fraction

and celestine (95.69 wt%), the potential for improvement is limited. Nevertheless, the density separation modelling data (Figure 9) confirms that is theoretically possible to concentrate the minerals of economic interest. The amount of Sr and celestine is highest in the 3.5–4.0 g/cm³ density fraction and is, at 46.33 wt% Sr, slightly higher than in the original bulk sample, which contained 45.57 wt% Sr. This improvement is also reflected by the increase from 95.69 wt% celestine in the bulk sample

to 97.81 wt% in the 3.5–4.0 g/cm³ density fraction. The mass percentage of each fraction is indicated above each density fraction on Figure 9. The 3.5–4.0 g/cm³ fraction represents 98.84 mass% of the bulk sample, indicating that there will be good recovery of the economic minerals and little waste to process.

The QEMSCAN® software, in combination with a well-developed database and element concentration calibrations, allow granulo-density and granulo-chemistry modelling to be

A geometallurgical approach to enhance the gravity beneficiation of a strontium deposit

performed. The results are important for simulation prior to actual ore processing tests. The concentrate is simulated from the feed materials by physical parameter processing before using more expensive processing techniques (*e.g.* hydro- and pyrometallurgy).

The software also allows a particle size distribution to be calculated, in which each particle size fraction of choice can be used for showing chemical and mineralogical compositions, as well as fractioned densities. This can save weeks of physical test work and provides process engineers with valuable information when performing and evaluating physical tests. Some selected results that could be important for celestine and Sr enrichment are presented in Figure 10 and Figure 11. Mass and mass percentages of Ca and Sr as function of density and particle sizes are shown. Mass of an element refers to the concentration of an element with respect to the overall sample. Mass percentage of an element refers to the concentration of an element in the respective size and density fraction. An element may, for instance, be highly enriched in a certain size or density fraction, the mass of which is small with respect to the overall sample. A low concentration in a fraction that represents a significant mass of the sample may dominate the overall mass balance of this element. Mass and mass percentage of Ca in the analysed sample are shown in Figure 10. The mass of Ca represents the concentration of an element with respect to the overall sample chemistry. The mass percentage of an element represents the concentration of an element with respect to the fraction chemistry without taking the relationship with the overall sample chemistry into account. The Ca mass in the sample is concentrated in the < 400 µm and < 4.0 g/cm³ fraction. In terms of mass percentage, the highest concentration of Ca occurs in the lower density fractions. As they are of minor significance with respect to the overall mass of the sample, these fractions contrast with the mass of Ca in the sample. The lower density fractions represent Ca partitioned in calcite and dolomite, whereas the higher density fractions

represent Ca in celestine. In the case of less concentrated samples, this information would help to decrease the amount of Ca by reducing the small size and low density fractions.

The same concept applies to the partitioning of Ba. It can be seen that the small size and low density fractions are enriched in impurities, unwanted elements, or minerals from celestine concentrates.

Summary and conclusion

Acid leaching processes are commonly applied to reduce elevated concentrations of Ca and Mg through carbonate dissolution. It can be shown that alternative methods, based on physical concentration of the ore, can be applied to reduce the concentrations of barium, magnesium, and calcium.

The presented example demonstrates the importance of automated mineralogy for the extraction of critical information for mineral processing of a celestine-rich strontium ore sample. Based on detailed mineralogical and microtextural analyses, it was possible to simulate how physical mineral separation can increase the quality of the concentrate. The QEMSCAN® model confirms that density separation can increase the concentrations of economic elements. The amount of Sr is highest in the 3.5–4.0 g/cm³ density fraction and is, at 46.33 wt% Sr, slightly higher than in the original bulk sample, which contained 45.57 wt% Sr. Barium occurs only in small amounts and cannot be decreased significantly. Using a simulated 3.5 g/cm³ cut-off density, the calcium content can be decreased in the heavy fraction from 0.87 wt% to 0.49 wt%. This is because the calcium-bearing minerals calcite and dolomite report to the light fraction. Granulo-chemistry modelling has shown that at a cut-off at 400 µm the calcium content can be reduced, but this will come at the cost of a significant loss of strontium.

Similar process modelling can be performed on any ore type for improving grades and recoveries of economically valuable elements by using chemical and physical differences
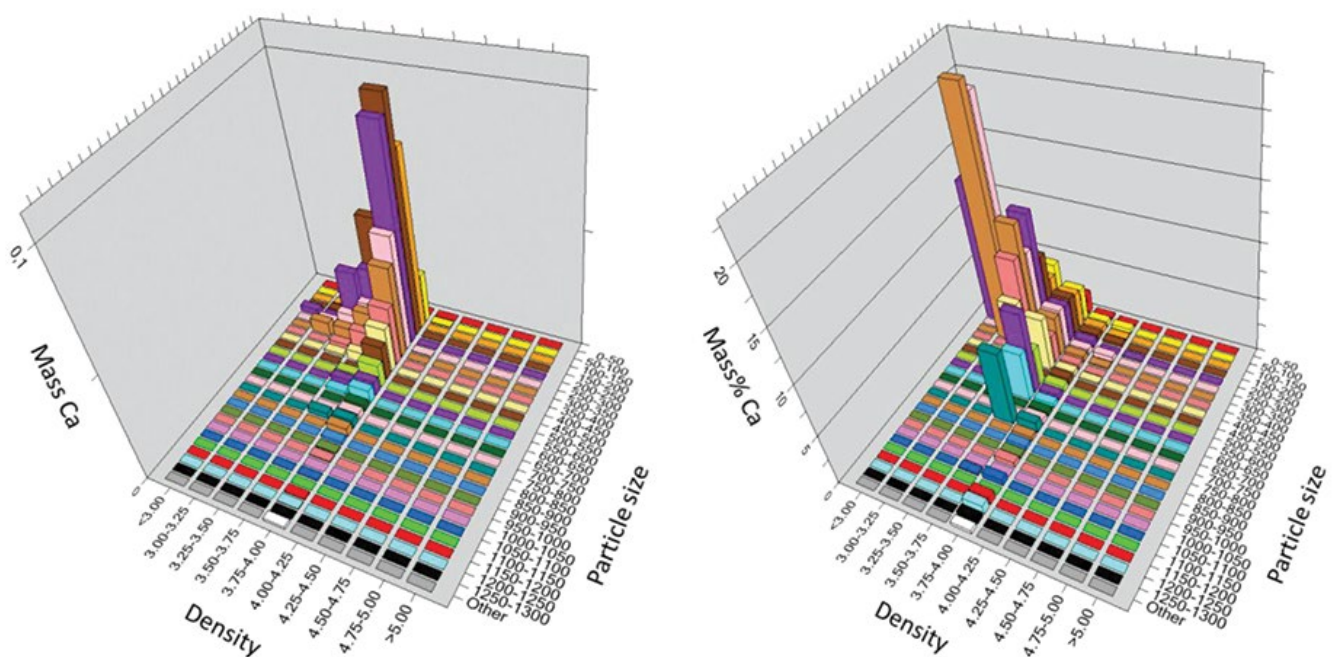

Figure 10—Ca partitioning in density and particle size fractions. The left hand diagram shows Ca concentrations with respect to the overall sample. The right hand diagram shows the Ca percentage in each fraction irrespective of the mass% of this fraction in the overall sample

A geometallurgical approach to enhance the gravity beneficiation of a strontium deposit
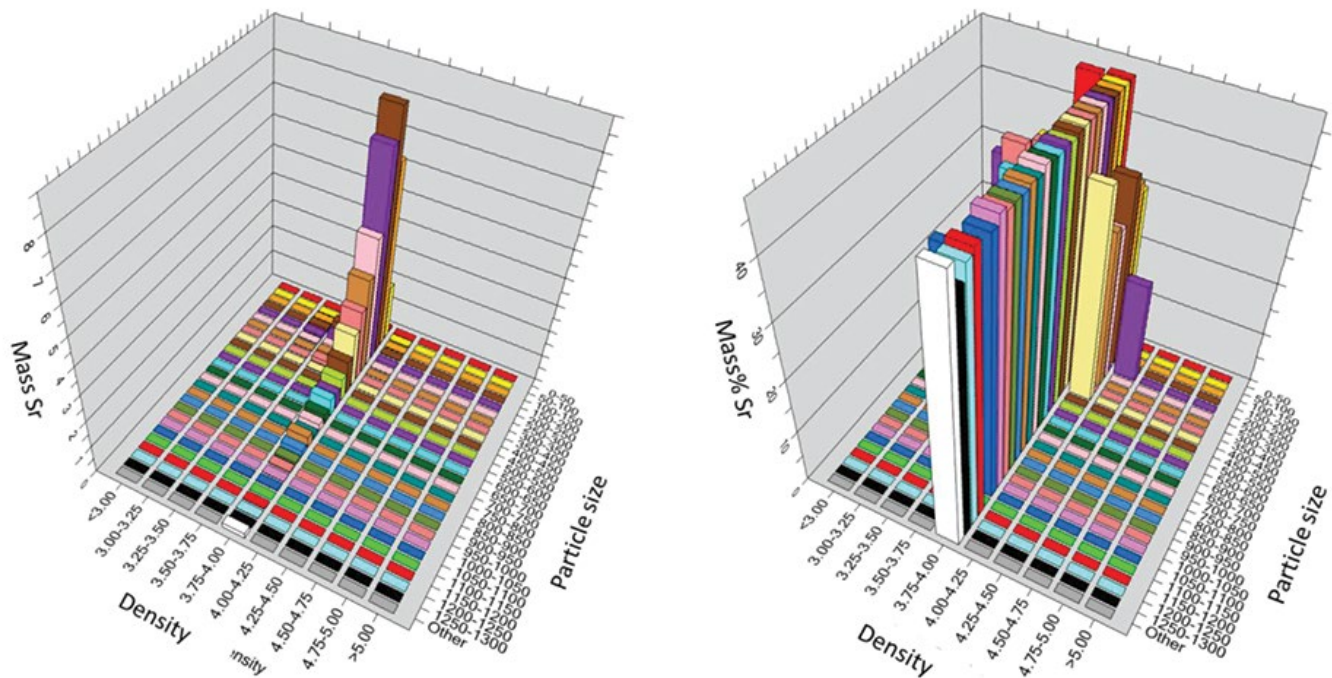

Figure 11—Sr partitioning in density and particle size fractions. The left hand diagram shows Sr concentrations with respect to the overall sample. The right hand diagram shows the Sr percentage in each fraction irrespective of the mass% of this fraction in the overall sample

of particles and minerals in particles. It must be kept in mind that the proposed process options are theoretical, and even sometimes hypothetical. Any proposed process option suggested by process modelling needs to be verified by physical tests, which are performed under real conditions that differ from ideal and computed modelling tests. The interactions of particles with different chemical and physical properties during mineral processing are important, difficult to simulate, and may lead to results that do not correspond to the modelling results. Nevertheless, the modelling provides a good starting point and roadmap guiding process engineers in performing their tasks. In the past, and even still nowadays, mineral processing tests were performed on an almost trial-and-error basis. Long testing cycles, accompanied by chemical analyses, which are not always immediately available, are time- and energy-consuming. This situation can be vastly improved by using automated mineralogy and geometallurgy concepts.

This study addressed the mine operator's major concerns:

➤ Minerals in the sample have been identified and their proportions calculated.
➤ Impurities have been precisely located. Barium is hosted mainly in celestine, replacing Sr. Calcite and dolomite host half the Ca present in the sample. The remainder of the Ca is hosted by celestine, replacing some of the Sr.
➤ A density separation has been proposed to enhance the valorization of the deposit by increasing the strontium content and decreasing the calcium concentration.

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