ON DIVERSE APPLICATIONS OF QEMSCAN IN THE OIL AND GAS INDUSTRY (AND BEYOND)

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ABSTRACT
Automated mineralogy identification, as implemented through QEMScan (quantitative evaluation of minerals by scanning electron microscopy) by FEI, is gaining wide spread interest in oil and gas applications. The experimental part of the method is focused on collection of the x-rays that are emitted when a surface is exposed to an electron gun of a scanning electron microscope. QEMScan distinguishes itself by the library, the so-called SIP (species identification protocol) file, and by the search routine that converts the collected X-rays to mineral maps. Extensive development of the SIP is necessary to encompass the, often complex, composition of e.g. clays encountered in many oil reservoirs. We present examples of such a development of SIP files relevant to specific clays and clastic rich carbonate reservoirs and show in studies of a broad spectrum of clays that often it is only very small changes in the acceptable amount of Mg^{2+}, Fe^{2+} and Al^{3+} that will lead to a positive identification. In pure carbonate settings the QEMScan methodology is primarily a source of 2D porosity as information on trace elements (concentrations less than 1 %) is not available from the low count spectra that form the basis for SIP identification. Our focus on bringing down the number of unclassified minerals in an image is not only achieved through SIP development; the sample preparation has also turned out to be of outmost importance. We present the optimal sample preparation conditions herein. The samples we are focusing on are plugs polished into thin sections and cuttings molded into epoxy and polished. Quite apart from reservoir rocks we have employed QEMScan to assist in mapping out trade routes from ancient pottery found in Qatar, whale shark skin and other relics such as sand from cemented dunes. We will assess the capabilities through these case studies and examples from field operations and demonstrate the powerful image processing in the Iexplorer package by also presenting grain size distributions and lithology results.

INTRODUCTION
The term QEMScan is a registered trademark of the FEI Company and stands for Quantitative Evaluation of Minerals by Scanning electron microscopy. It enables generation of the 2D mineralogical composition across a rock surface by rastering the sample through the electron beam. It is in essence a library match of the emitted X-rays to a library of X-ray spectra. Once an electron hits the surface it can do one of three things:

1. Back-scatter off the surface
2. Generate a secondary electron
3. Excite the surface material with subsequent generation of an X-ray photon when the surface relaxes to the ground state.

It is the spectrum of the emitted photons in combination with the back-scattered electrons that is employed in the mineralogical surface characterization. The apparatus can provide high resolution SEM images (down to 1.1 nm) in combination with mineral maps with a resolution of 1 μm. The reason why the resolution differs for SEM and QEM is related to the sample area probed in the two methods; secondary electrons can only efficiently be produced from the top few layers of the sample as they would otherwise be blocked by the surrounding sample molecules whereas X-rays can probe a much deeper position of the sample and thus a much larger area. The mineral identification process is carried out with the so-called spectral engine in the FEI Iexplorer package where the key tool is the Species Identification Protocol (SIP); a library with all the necessary X-ray data to match the experimental spectra. The process takes its starting point in a low-count (1000 photons) spectrum to save time. This means that decent sampling statistics are needed to make a correct classification of species such as trace elements. The spectrum is divided into energy regions and each element or mineral in the SIP is classified by sets of count number and energy. The mineralogy at a specific point is then identified by generating a superposition of the spectra in the SIP to match the experimental spectrum. The search procedure relies on a careful SIP preparation so that the match is done in "a first come first serve" manner. The end result is a full 2D mineralogy map of the sample.

A literature review of QEMScan applications shows that the method has been applied in other industries over the past decade. Examples include the study of *coal combustion* [1-3], *characterization of metal ores* [4-7], various *geoscience applications* [8], *archaeology* [11], and *toxicity evaluations* [12]. Within the oil and gas industry, the main application so far has been focussed on characterization of shales [13], although recently the technique is beginning to be applied also for other reservoir types [14-16].

After having outlined what we have found to be the best practice for sample preparation we explore the use of QEMScan for a variety of purposes. Firstly, we will explore the need for SIP development in three different formation types (carbonate, clastic and shale). Secondly, we will exemplify with a few practical oil-field related examples. Thirdly, we will focus on more refined applications such as those giving size distributions in cutting samples or on how to provide an assessment of a petrophysical parameter such as porosity.

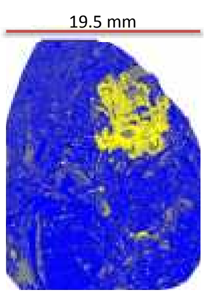
QEMScan experimental, best practice sample preparation and its consequences

All our experiments herein are performed with a 650F instrument from FEI equipped with two EDS detectors at 15 keV. The data are processed with the Iexplorer software package.

The primary concern in automated mineralogy experiments is in most cases the number of unclassified pixels, we have experienced anywhere between 0 and 70 % unclassified in our QEM experiments. There are several factors that can contribute to a high unclassified count; one is sample preparation. The lower limit on the QEMScan resolution is about 1 μm but often, particularly in clays, the crystallites are significantly smaller. This gives rise to the registration of more than one spectrum in a single pixel and thus a spectral pattern that cannot be easily reconciled with a single mineral. The result is a pixel that will be labelled as unclassified. This can be alleviated to a certain extent by software processing but is at the end of the day intrinsic to the sample. A similar effect is in play when the sample is not sufficiently cleaned or when the surface is not smooth enough. In these latter cases improvement is possible through more careful sample polishing. In our system the samples can be introduced in three manners; as an odd sized specimen, as a thin section or as cast into epoxy for subsequent cutting and polishing. The epoxy moulding also requires a fair amount of attention. For example air bubbles will have the same effect as impurities and therefore it is important to degas the epoxy ingredients and the samples before mixing.

Three applied examples of SIP development in oil and gas

As a starting point we have taken the standard version of the SIP list that is provided with the FEI instrument. It is referred to as the O&G 15kV v3.7. This list is then modified for the various needs in the present work. For carbonate rocks no modification is needed as can be seen in Fig. 1. Measurements on two different thin section areas (19.5 mm&7.5 mm) give rise to hardly any unclassified pixels (0.18 %&0.18 %, respectively). The quantification shows (65.1 %&60.0 %) calcite (8.4 %&18.7 %) pyrite and (26.3 %&21.2 %) porosity. The differences show that the sample macroscopically is quite heterogeneous and that the location of the sampled area matters. The estimated porosity value is in line with the results of an MICP study [54, 55]. The 7.5 mm sub-area has a smaller pixel spacing and it can be seen that the pixel spacing does not impact the classification significantly in this case. The primary reason for this is that the sample is homogeneous at this resolution scale and consists of primarily large crystallites.



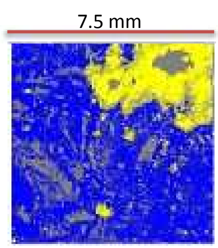


Fig. 1. QEMScan images on carbonate thin sections with a 10 μm point spacing (left) and a 1 μm point spacing (right).

There is a significantly more pronounced need for SIP development when moving away from carbonate reservoirs. An example is given in Fig. 2 where the result of a series of measurements on cuttings material from a more complex formation is shown. The first panel shows the result of an intermediately cleaned sample, the second panel shows one that has been run at higher resolution and more carefully cleaned and finally the third panel shows the result of carefully cleaned and polished sample. It can be seen that there are several factors in play to achieve a good result and that the number of unclassified pixels can be significantly reduced by proper sample treatment.

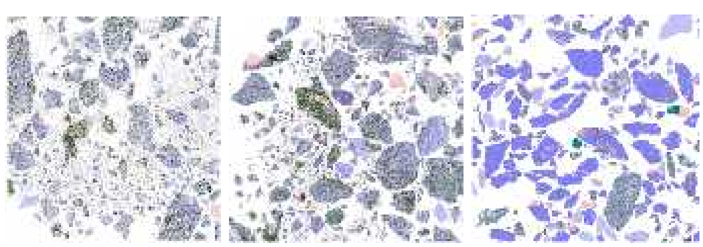


Fig. 2. QEMScan images of cuttings from complex reservoir. Each color corresponds to a distinct mineral. Black corresponds to unclassified pixels and white is background.

Fig. 2 clearly show the usefulness of QEMScan for cutting analysis during drilling. One can quite easily imagine the added value in for example a logging-while-drilling application of QEMScan where the various geological layers can be monitored and it can thus be assured that the drilling takes place into the correct formation.

The conventional reservoir rocks that have been discussed hitherto lend themselves to QEMScan analysis quite easily. However, the actual geological information is limited as the rock consists entirely of calcite. The situation is different for unconventionals such as oil shales (Fig. 3). In that case the mineralogy is very diverse as can be seen from Fig. 3 where different clay minerals are predominant. What is quite surprising for the oil shale in Fig. 3 is that the standard library more or less got it right with only 0.29 % unclassified pixels. It should however in all fairness be mentioned that the image has been treated with one of the clever preprocessors in Iexplorer, the touching particles preprocessor that ensures a reassessment of an unclassified pixel to a mineral if it is surrounded by three identical pixels. Prior to treatment, the unclassified pixel count amounted to ca 8 %.

Fig. 3. QEMScan image of an oil shale treated with the touching particles preprocessor.

It is not in all shale cases that the unclassified pixel count can be reduced as described above. An example is shown below where the initial identification with the standard library gave 70 % unclassified pixels (Fig. 4 left). A very simple modification of the library to accommodate for a smectite which in this case deviates from the library smectite by having more iron and magnesium (tolerance increase 2 and 1 %, respectively) and less aluminium and silicon (tolerance decrease 5 and 4 %, respectively).

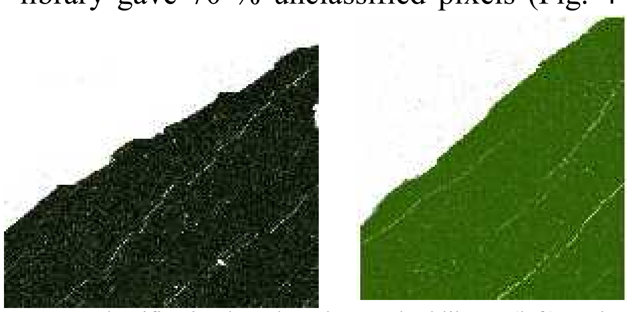


Fig. 4. Classification based on the standard library (left), and a slightly modified SIP file where content of Fe and Mg is slightly higher but where the Al and Si content is lower.

The methodology for modifying the library is not only valuable in identifying the detailed mineralogy of shales. We have also employed the methodology in an oil-field related case where only amorphous salts are present. In a plant for purification of seawater that relies on the oxidation of chloride to hypochlorite it turned out that a white precipitate was formed. It is a huge benefit not having to transport the side product to shore. So we used the QEMScan images shown in Fig. 5 to verify that the waste products can safely be disposed of into the ocean. Due to the amorphous nature of the salts XRD would not have been a suitable way to perform the analysis.

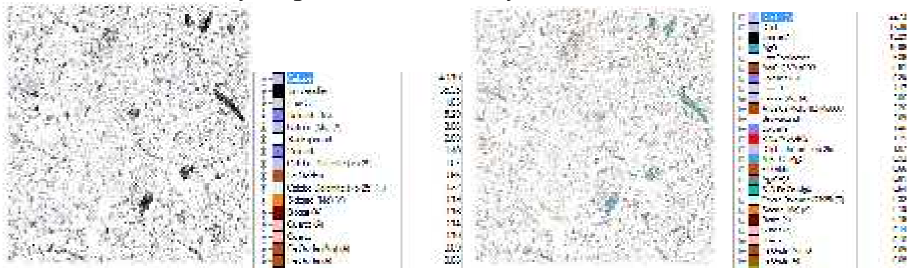


Fig. 5. QEMScan images showing a high about of unclassified (left) before SIP development (right). The unidentified salts in the production system are primarily oxides and hydroxides that can be safely disposed of into the sea.

Porosity from QEMScan

Quite apart from the mineralogy there is also significant added value in assessing the sample porosity. QEMScan offers a convenient independent way of measuring this important petrophysical parameter. In Fig. 6 is shown the porosity as a function of depth in a certain well.

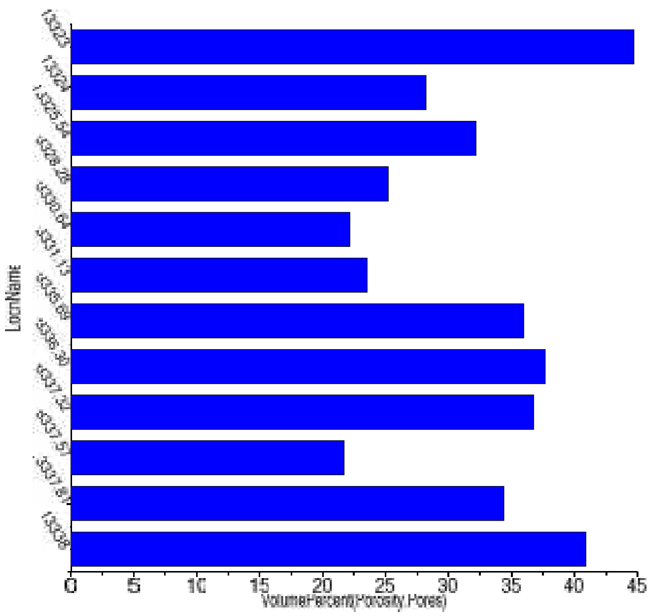


Fig. 6. Plot of well depth versus total porosity as measured from QEMScan. The plotting routine is quite convenient in Iexplorer.

Size and mineral distributions

When sampling for the mineralogy one also can derive the circumference of the individual particles in a cuttings sample and Iexplorer will generate a plot that shows the size of each particle. This graph can then be converted to ASCII to develop distribution functions of particle sizes in all sorts of particulate matter. With SIP development it is also possible to map specific minerals in the same manner.

CONCLUSION

The applications of QEMScan in oil and gas are very diverse. The key to success in terms of achieving full classification, i.e. no unclassified pixels, is to pay great attention to the sample preparation (primarily surface smoothness) and the SIP development. The SIP development is sensitive to even small changes in the various constituents of e.g. shales. When that is under control the QEMScan methodology is applicable to carbonates, shales and even ancient Qatari pottery for determination of origin.

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REFERENCES

1. Buhre, B. et al. Factors affecting the vaporisation of silica during coal combustion. *Fuel Proc. Tech*. (2007) 88: 157-164.
2. Golab, A. et al. High-resolution three-dimensional imaging of coal using microfocus X-ray computed tomography, with special reference to modes of mineral occurrence. *Int. J. Coal Geol.* (2013) 113: 97-108.
3. Klopper, L. et al. Influence of added potassium and sodium carbonates on CO2 reactivity of the char from a demineralized inertinite rich bituminous coal. *J. Anal. Appl. Pyrol.* (2012) 96: 188-195.
4. Andersen, J.C.Ø. et al. Use of QEMScan for the characterisation of Ni-rich and Ni-poor goethite in laterite ores. *Minerals Eng.* (2009) 22: 1119-1129.
5. Ghorbani, Y. et al. Use of X-ray computed to investigate crack distribution and mineral dissemination in sphalerite ore particles. *Minerals Eng.* (2013) 43: 44-51.
6. Goodall, W.R. Characterisation of mineralogy and gold deportment for complex tailings deposits using QEMScan *Minerals Eng.* (2008) 21: 518-523.
7. Lotter, N.O. et al. Modern process mineralogy: Two case studies. *Minerals Eng.* (2011) 24: 638-650.
8. Allen, J.L. et al. New technology and methodology for assessing sandstone composition: a preliminary case study. *Geol. Soc. Am. Spec. Papers* (2012) 487: 177-194.
9. Ghorbani, Y. et al. Use of X-ray computed tomography to investigate crack distribution and mineral dissemination in sphalerite ore particles. *Minerals Eng.* (2011) 24: 1249-1257.
10. Nie, J. et al. Controlling factors on heavy mineral assemblages in Chinese loess and Red Clay.*Pal. Pal. Pal.* (2013) 381-382: 110-118.
11. Knappett, C. et al. Mineralogical analysis and provenancing of ancient ceramics using automated SEM-EDS analysis (QEMScan): a pilot study on LB I pottery from Akrotiri, Thera. *Arch. Sci.* (2011) 38: 219-232
12. Williamson, B.J. et al. Automated mineralogical analysis of PM10: new parameters for assessing PM toxicity. Environ. Sci. Technol. (2013) 47: 5570-5577.
13. Knackstedt, M. et al. Integrating reservoir characterization: 3D dynamic, petrophysical and geological description of reservoir facies. SPE 133981.
14. Solling, T. et al. Multiscale characterization on the pore network in carbonate rocks. SPE 166023.
15. Knackstedt, M. et al. Rock typing across disciplines. SPWLA 2010.
16. Lemmens, H.J. et al. FIB/SEM and SEM/EDX: a new dawn for the SEM in the core lab? *Petrophysics* (2011) 52(6): 452-456.