21 Microscopy and X-Ray-Based Analytical Techniques for Identifying Mineral Scales and Deposits

Valerie P. Woodward and Zahid Amjad

CONTENTS

21.1 INTRODUCTION

In many industrial processes, the feedwater used contains mixtures of dissolved ions that are unstable with respect to precipitation. Various factors such as pH, temperature, type and concentration of dissolved ions, flow velocity, and equipment metallurgy contribute to the precipitation and deposition of sparingly soluble salts on equipment surfaces. The class of crystalline and amorphous compounds formed in industrial water systems generically known as scale and deposits has a widespread importance across a variety of disciplines, as can be seen from other chapters in this book and from other books [1–3]. Scale is defined as the deposit of certain sparingly soluble salts such as calcium carbonate, calcium phosphate, calcium oxalate, magnesium hydroxide, and calcium sulfate, from the process fluids after precipitation onto the tubing and other process surfaces. The commonly encountered deposits

in industrial water systems include carbonates, sulfates, and phosphates of alkaline earth metals, silica, magnesium silicate, corrosion products, microbiological mass, and suspended matter. These deposits, especially on heat transfer surfaces in thermal distillation, cooling, and boiler systems, lead to overheating, loss of system efficiency, unscheduled shutdown, and untimely heat exchanger failure. In desalination by reverse osmosis (RO) process, deposition of unwanted precipitates may result in poor water quality and premature membrane failures. Deposition of scale in some cases may be beneficial as in the case of drinking water transmission lines wherein the layer of scale deposit protects the piping from corrosion by isolating it from the water. However, in most cases, scale is undesirable as it adversely affects the overall efficiency of the process.

Over the last three decades, considerable experience has been gained through the examination of failed heat exchangers and RO membranes; in that process deposit characterization has been performed on heat exchangers of different metallurgies and nearly every type of RO membranes including spiral-wound, tubular, and hollow fiber configurations. In addition, autopsies of membranes of different compositions such as cellulose acetate, cellulose triacetate, and thin-film composite polyamide have been carried out using different analytical techniques for identifying possible cause(s) of membrane failure and deposit composition. The information collected through deposit characterization has enabled the academic researchers and industrial technologists to develop new scale inhibitors, dispersants, and membrane cleaners. This chapter addresses the use of several analytical techniques to characterize the type, crystalline structure, and composition of mineral scales and deposits. In addition, these techniques can also be used to identify the cause(s) of heat exchanger and membrane failures in the industrial water systems.

21.2 ANALYTICAL TECHNIQUES FOR IDENTIFYING MINERAL SCALES AND DEPOSITS

A number of methods may be employed to characterize mineral scales (i.e., sparingly soluble salts such as calcium carbonate, calcium phosphate, calcium oxalate, magnesium hydroxide, and calcium sulfate) and deposits (i.e., rust, clay, and zinc oxide). Some of these methods are listed in Table 21.1, along with the type of information obtained and their advantages and disadvantages.

The following sections discuss various analytical techniques used to characterize commonly encountered scales and deposits. There is also a brief description of the other methods used in support of the deposit characterization, although it will not be as extensive as those previously listed. These analytical techniques include

- Optical microscopy
- Scanning electron microscopy and energy dispersive x-ray spectroscopy (SEM/EDS)
- Wide-angle x-ray diffraction (WAXD)
- Particle size (PS) analysis

TABLE 21.1
Analytical Methods for Water Treatment Precipitates and Deposits

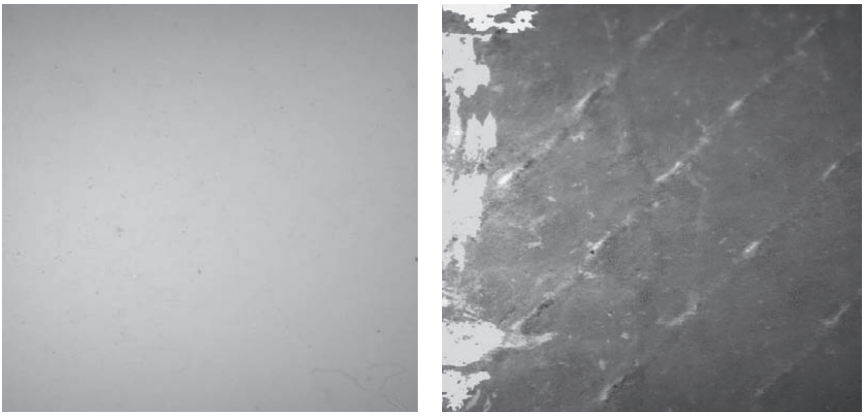
Technique	Information	Advantages	Disadvantages
Optical microscopy	M	Cost, time	Limited information
SEM	M, S	Time, sample size	Cost
ICP	E	LDL	Sample size, prep time
Infrared	C	LDL, time, cost	Interpretation
Transmitted	C	LDL, time, sample size	Prep, sample must be homogenous
Reflected	C	Time, sample prep	Flat smooth surfaces must be homogeneous
EDS	E	Time, sample size	LDL
XPS	E, C	LDL, surface sensitivity, chemical states	Cost, interpretation
WAXD	C	Time, phase identification	Cost, sample size
PS analysis	S	Time, cost	Size range limitations per instrument type, particles must stay suspended

E, elemental; M, morphology; C, composition; S, size; LDL, lower detectable limit.

21.2.1 Optical Microscopy

Direct observation of system components (membranes, filters, parts of treatment systems) is the first step in characterizing a failure or process. This is simply accomplished in most cases with the use of a stereomicroscope. One can observe extent of scale coating, degree of corrosion in metal parts, color differences, and shape and size differences, among other attributes. Accompanied by a digital microscope camera, the stereomicroscope is a powerful, rapid classification tool and can sometimes provide enough information that other microscopy techniques may be rendered unnecessary. Figure 21.1A and B show the obvious differences between a new, clean membrane and one that has been fouled with iron oxide.

The sample can be examined using a stereomicroscope or a compound optical microscope, both of which can have transmitted and reflected light sources. Compound optical microscopy can be used to obtain color, size, crystalline structure, refractive index, and other information about water-formed deposits. One of the most powerful tools in optical microscopy is polarized light illumination for particle classification. Many materials have distinct properties in polarized light—color, brightness, refractive index, and crystalline habits are only a few. These properties can be unique to specific materials and can serve as benchmarks for the experienced microscopist. Figures 21.2 through 21.5 illustrate the unique appearances of calcium carbonate, calcium sulfate, clay, and iron oxide. The brightness (birefringence) and high refractive index of calcium carbonate and calcium sulfate, the color of iron



(A) (B)

FIGURE 21.1 Stereomicroscope images of new and fouled membranes: (A) is the new membrane and (B) is the fouled membrane (nominal 13×).

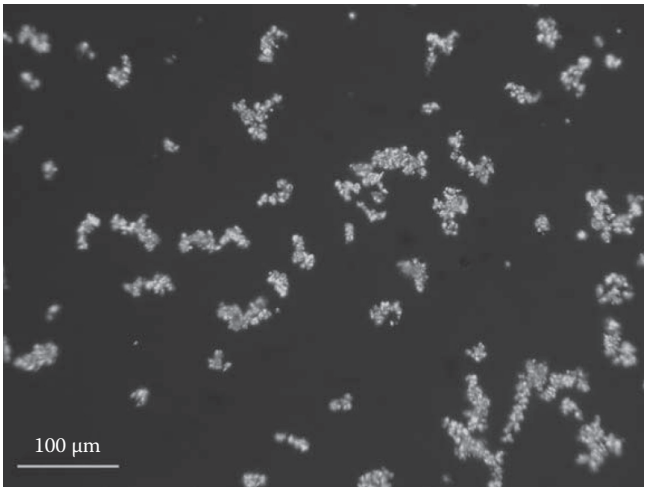


FIGURE 21.2 Transmitted polarized light micrograph of calcium carbonate (nominal 370×).

oxide, and the diffuse fine-particle nature of the clay are distinctive benchmarks that can guide the microscopist in identifying deposits.

Transmitted light observation can also be used to do microchemical spot tests to identify cations and anions if one does not have immediate access to SEM/EDS. A very common test for calcium carbonate is the addition of a droplet of 10% aqueous hydrochloric acid to a dry deposit sample to determine the presence of carbonate salts. The carbon dioxide evolution from carbonates occurs in the form of bubbles. Some disadvantages of optical microscopy include limited depth of focus, especially in reflected illumination, magnification limitations (~1 µm resolution), and lack of direct elemental information. When these limitations are encountered, SEM/EDS is the next logical

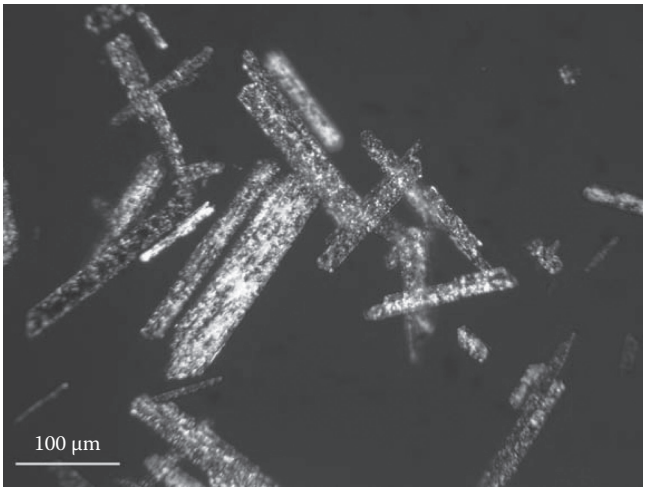


FIGURE 21.3 Transmitted polarized light micrograph of calcium sulfate (nominal 370×).

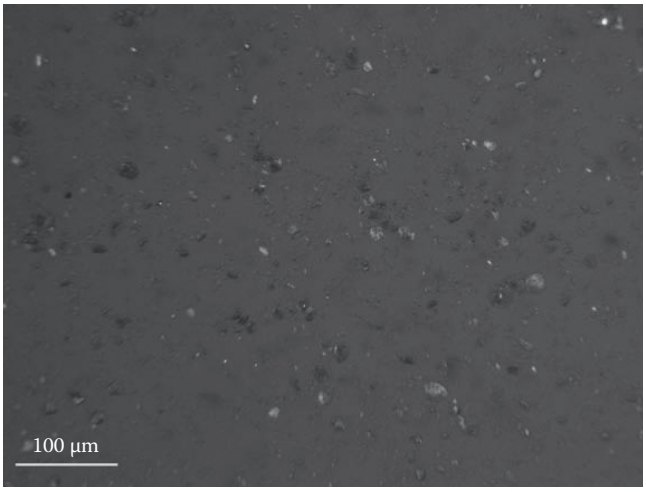


FIGURE 21.4 Transmitted polarized light micrograph of clay (nominal 370×).

step in the analytical scheme. Currently, most optical microscopes are equipped with digital cameras specifically designed for microscope use. The cameras are accompanied by powerful capture and processing software, making acquisition, manipulation, storage, and usage of high-quality photomicrographs rather commonplace.

21.2.2 Scanning Electron Microscopy

The SEM is the next logical tool in the microscopy analysis scheme after optical microscopy. The SEM provides excellent depth of field, a very large magnification

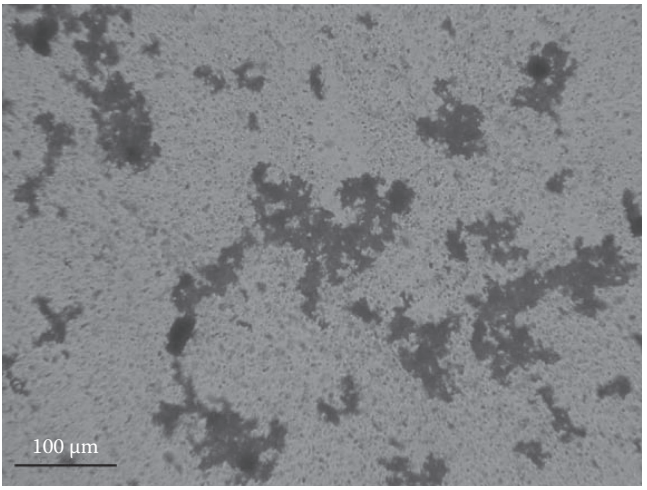
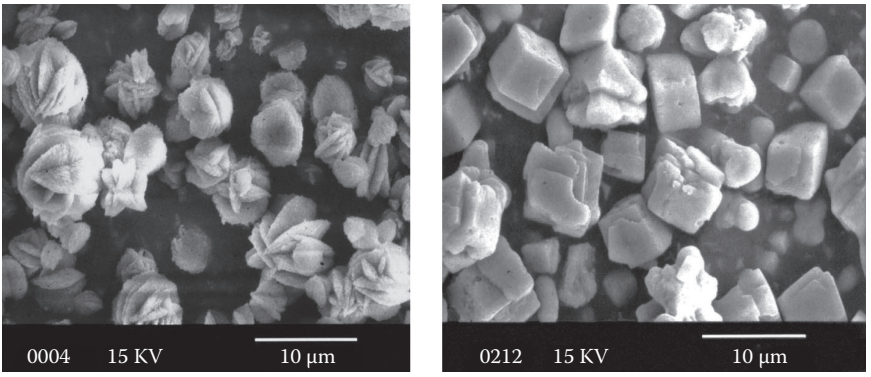


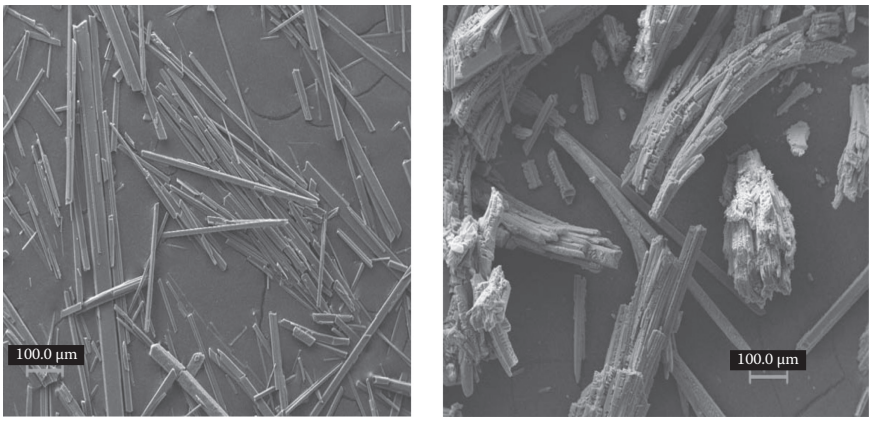
FIGURE 21.5 Transmitted polarized light micrograph of iron oxide (nominal 370×).

range, several detection modes and flexible analysis environments, as well as a means to elemental analysis. PS, shape, crystal habits, packing tendencies, and degree of agglomeration are all characteristics that can be elucidated via SEM imaging. A particularly informational usage of the SEM is tracking morphology changes of mineral scale such as calcium carbonate. A series of stand-alone deposit particles or particles collected on filters during laboratory evaluation of water treatment products can be compared for all of the previously noted attributes, as well as for changes in particle population. Figure 21.6A and B are examples of two different $CaCO_3$ polymorphs, namely, vaterite and calcite. Figure 21.7A and B are typical secondary electron (SE) images of $CaSO_4$ deposits formed in the absence and presence of inhibitor; the key observation is the change in the morphology and size of the crystals. Figure 21.8A



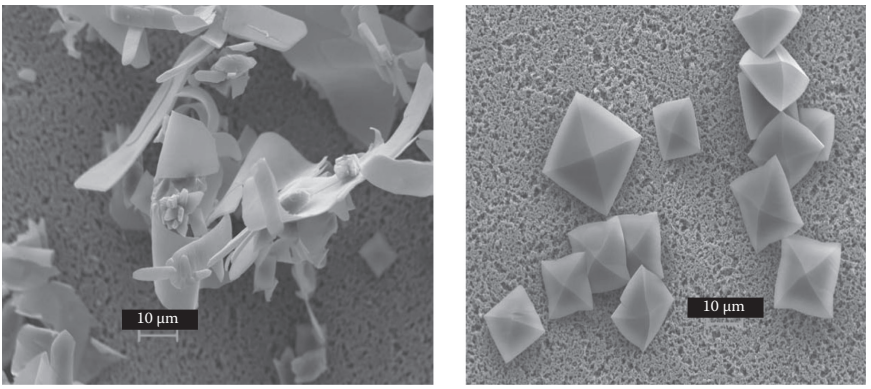
(A) (B)

FIGURE 21.6 SEM micrographs of two different calcium carbonate polymorphs: (A) is vaterite and (B) is calcite.



(A) (B)

FIGURE 21.7 SEM micrographs of calcium sulfate pre- and posttreatment with poly(acrylic acid): (A) is the material formed in the absence of inhibitor and (B) is the material formed in the presence of 1 ppm inhibitor.



(A) (B)

FIGURE 21.8 SEM micrographs of two types of calcium oxalate: (A) is the monohydrate formed in the absence of inhibitor and (B) is the dihydrate formed in the presence of 1 ppm inhibitor.

and B show different morphologies of calcium oxalate crystals resulting from the absence or presence of an inhibitor. In the absence of an inhibitor, the crystals formed are calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$); however, the presence of 1 mg/L of Carbosperse™ K-732, a low molecular weight poly(acrylic acid), favors the formation of calcium oxalate dihydrate ($CaC_2O_4 \cdot 2H_2O$). Calcium oxalate scale, also known as "beer stone," is generally encountered in the brewing industry.

Current SEMs are entirely digital and allow simple acquisition and storage of electronic images. Electronic image formats also allow ease of post-processing, embedded annotation, and simple transfer into electronic documents. Another important aspect of the digital SEM is that the majority or all of the operations are performed

via software. Until about 20 years ago, commercial SEMs were only available in the high-vacuum mode. High-vacuum SEMs required that the samples were dry and coated with a conductive metal or carbon to prevent charging (poor conduction of the electron beam). Current SEMs are also available in high-pressure modes (also called variable pressure, low vacuum, etc., depending upon the manufacturer) and "environmental" modes (ability to image liquid water at room temperature). Both of these modes allow the analyst to observe uncoated samples or materials that are not completely dry.

SEM imaging and EDS elemental analysis are made possible by the interaction of a high-energy electron beam with a sample. Numerous types of interactions occur, mostly in the top 10 or so micrometers of a sample in 3-D. The interactions of importance are those that allow the emission of secondary electrons (SEs) or backscattered electrons (BSEs) (imaging, atomic number contrast) and primary x-rays (elemental analysis). Most morphology imaging is performed in the SE mode. The actual depth of penetration of the electron beam is dependent upon the accelerating voltage of the electron beam and the average density of the specimen, with higher accelerating voltage and lower specimen average density yielding greater depth of penetration. The accelerating voltage relationship can be exploited to obtain surface information (lower voltage) or subsurface information (higher voltage). SE imaging can be performed in high-pressure modes as well as high vacuum with the advent of improved detectors made specifically for collection of SEs in the high-pressure environment. The majority of the images presented in this chapter were obtained between 15 and 20 kV accelerating voltage on metallized specimens in a high-vacuum mode.

The BSE mode provides information from depths below that from which SEs are generated and is sensitive to the average atomic number of the specimen if there is not much surface topography. BSE mode can be helpful in imaging samples that charge in high vacuum even when coated, and in locating higher atomic number particles on lower atomic number substrates. The former use of BSE is not so important if one has a high-pressure microscope. The latter method is extremely helpful when attempting to locate small particles in a low concentration on filters. Many times the particles of interest and filtration debris cannot be distinguished from each other morphologically and can only be confirmed using EDS; however, performing EDS analysis on a number of tiny particles can be tedious. In the BSE mode, S-, Ca-, and Fe-containing particles will present themselves as brighter spots or areas on the darker filter background and make isolation for EDS analysis rather facile. Figure 21.9 illustrates typical BSE imaging of mixed particles of calcium carbonate, calcium sulfate, and iron oxide on a filter for the purpose of particle-type location. There are times when particle populations are quite sparse and manually searching the filter surface in the SE mode is time consuming. Using BSE to "light up" the particles that have significant average atomic number differences from the filter allows the analyst to go directly to a brighter spot and then spend quality analysis time to determine the particle morphology and elemental composition. Improvements in BSE detector technology in the past 10–15 years allow the analyst to effectively use the technique with low SEM accelerating voltages and probe currents, subsequently leading to

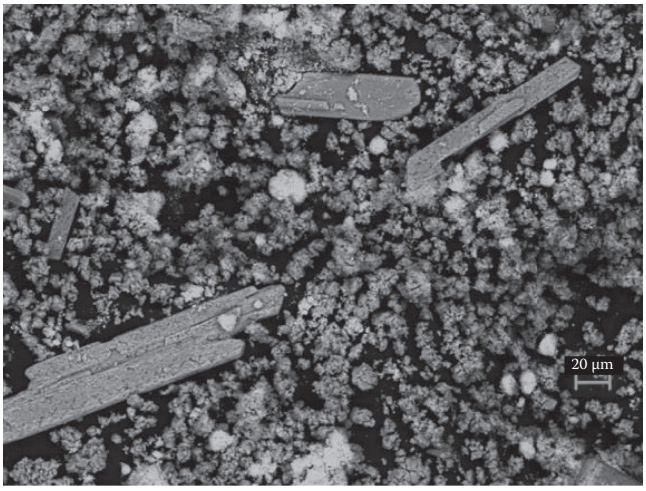


FIGURE 21.9 SEM micrographs of calcium carbonate, calcium sulfate, and iron oxide in BSE contrast mode to facilitate different compositions of particles on substrate.

better imaging, and afford much higher Z-resolution so that grayscale differences among particles, areas, or features are more informational.

21.2.3 Energy Dispersive X-Ray Spectrometry Analysis

One of the more valuable assets of the SEM is the ability to obtain elemental composition information from materials. Characteristic x-rays from elements are generated at a depth below that from which BSEs are generated; as in the imaging method, that depth can be affected by the accelerating voltage of the electron beam and the density of the specimen. EDS analysis can be used to obtain compositional information on quasi-bulk specimens (low SEM magnification, high accelerating voltage) or on specific particles, morphologies, or isolated areas on filters or within deposits.

Historically, detectors were protected from the SEM chamber environment with a thin window of beryllium, which limited the detection of elements to atomic number 10 (sodium) and above. Most current EDS detectors are able to detect boron and in some cases beryllium, by the use of a thin polymer window between the chamber environment and the detector crystal. In addition to qualitative identification of the very low atomic number (low Z) elements, the thin-window detectors also allow improved quantitative analysis of elements such as sodium and magnesium by virtue of improved signal-to-noise ratio in that area of the spectrum. The latest development in detector technology is the silicon drift detector (SDD). The SDD is a solid-state detector that allows for much higher count rates than the standard lithium-drifted silicon, or Si(Li), detector with equivalent resolution, rapid x-ray mapping, and electronic cooling (vs. liquid nitrogen cooling with Si[Li]). Detection and quantification of lower atomic number elements can also be improved by the use of lower accelerating voltages, which confine excitation to elements in that range of energies. Figures 21.10 and 21.11 are typical

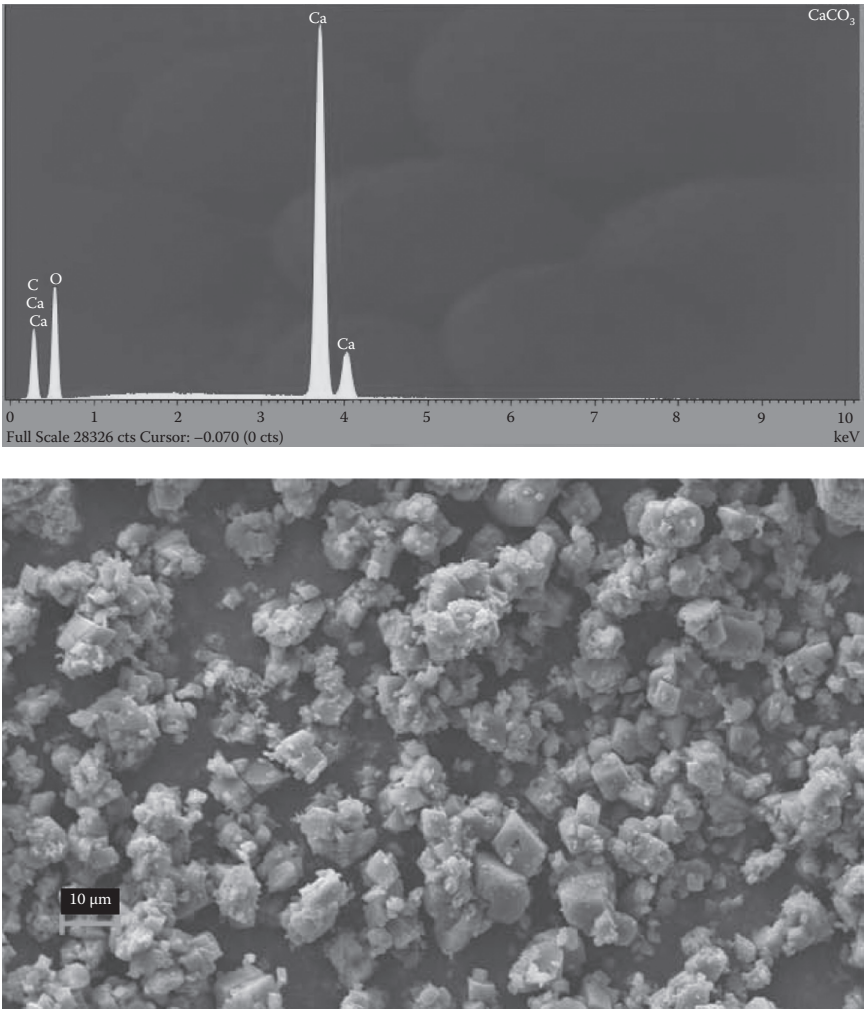


FIGURE 21.10 Typical EDS spectrum of calcium carbonate and SEM micrograph of sample from which EDS spectrum was generated.

EDS spectra and accompanying SEM images of $CaCO_3$ and clay collected with a thin-window SDD detector. Figure 21.10 illustrates $CaCO_3$ with a crystalline morphology and its typical EDS spectrum at 20 kV accelerating voltage. Figure 21.11 illustrates aluminosilicate clay and its typical EDS spectrum. In both EDS spectra, the peak intensity for oxygen is not intuitively proportional to the empirical value as one would conjecture, considering that oxygen is ~48 wt.% of $CaCO_3$ and ~46% for the clay; however, the x-ray yield for very low-Z elements is affected by a number of factors including PS. If one were doing quantitative analysis, the algorithms used would take into account the x-ray line properties and the SEM conditions to correct for the low-Z yield.

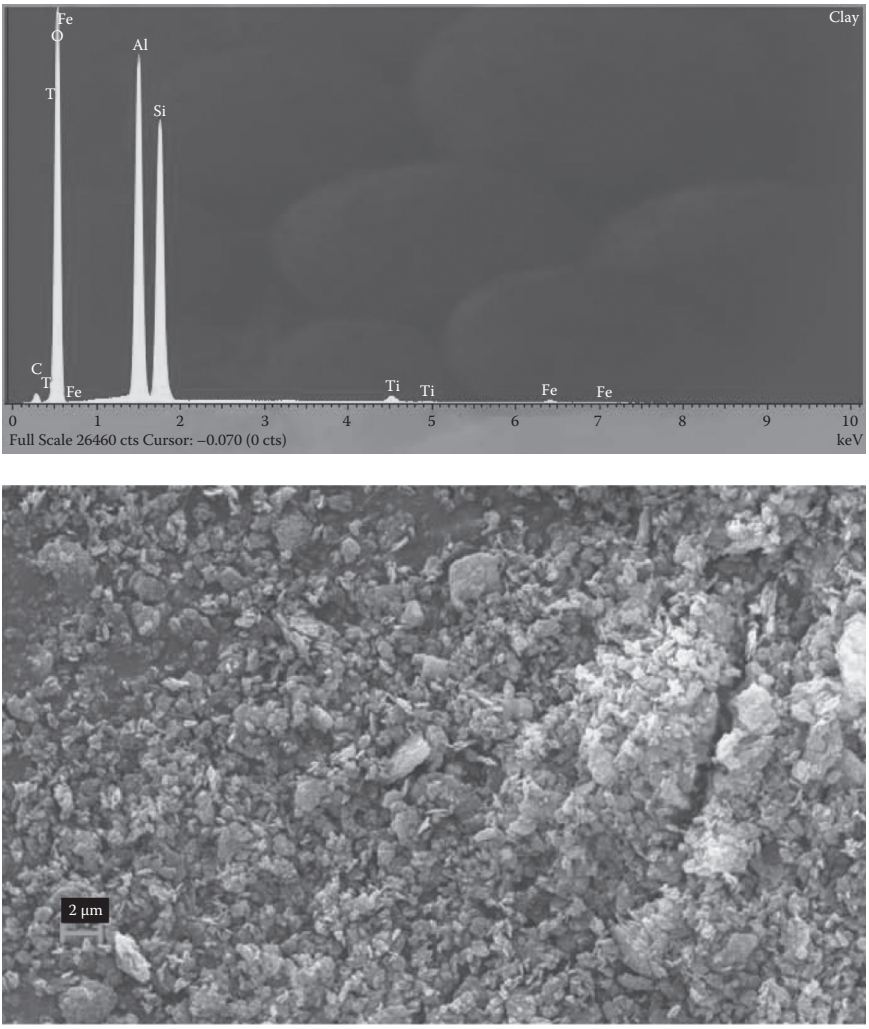


FIGURE 21.11 Typical EDS spectrum of clay and SEM micrograph of sample from which EDS spectrum was generated.

X-ray mapping (element maps) is a powerful tool that EDS analysis affords the scientist. This method combines the digital secondary imaging of the SEM with the accompanying element distributions within that image. Where backscattered contrast in the SEM can provide inferential information about atomic number differences (i.e., the brightest particles are the highest Z, the darkest ones are the lowest Z), x-ray maps are unequivocal regarding the composition at a specific feature. Figure 21.12 is an x-ray map montage of the mix in Figure 21.9 that was rendered in BSE; the maps provide specific element distributions where the BSE image is informational, but less specific. Also part of current commercial EDS analysis packages is the ability to store spectra generated at each pixel of an x-ray map. This allows for

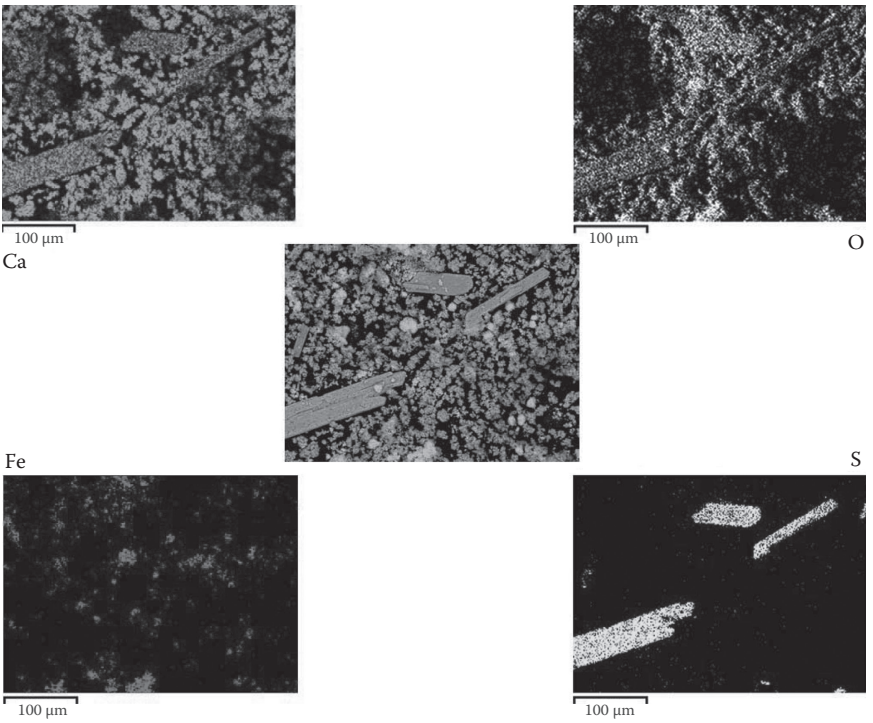


FIGURE 21.12 EDS elemental map montage of calcium carbonate/calcium sulfate/iron oxide mix from Figure 21.9.

post-acquisition compositional analysis of particles, areas, or other features within an x-ray map using routine computer mouse manipulations.

Under certain conditions EDS analysis can be quantitative as well as qualitative. For routine use, those conditions include homogeneous specimens, specimen thickness that is "infinite" to the beam penetration, relatively flat surfaces, and beam geometries that favor optimum collection of x-rays by the EDS detector. SEM column conditions are used by the EDS analysis programs in the correction algorithms; modern EDS analyzers can be integrated with digital SEMs so that information can be collected and stored automatically with the spectra; older instruments require the analyst to store the acquisition information manually with the spectra. There are also special conditions and programs that are required for quantitative analysis of individual particles, extremely small phases, and thin films, but those are not typically used in the characterization of water treatment precipitates and deposits.

21.2.4 Wide-Angle X-Ray Diffraction

While EDS analysis in the SEM can provide elemental information about scales and/or deposits, there are times when it is necessary to know the form in which the materials exist. As an example, an EDS spectrum alone can indicate that there is C, O, and Ca in a deposit; however, it is necessary to know whether that is $CaCO_3$, CaO

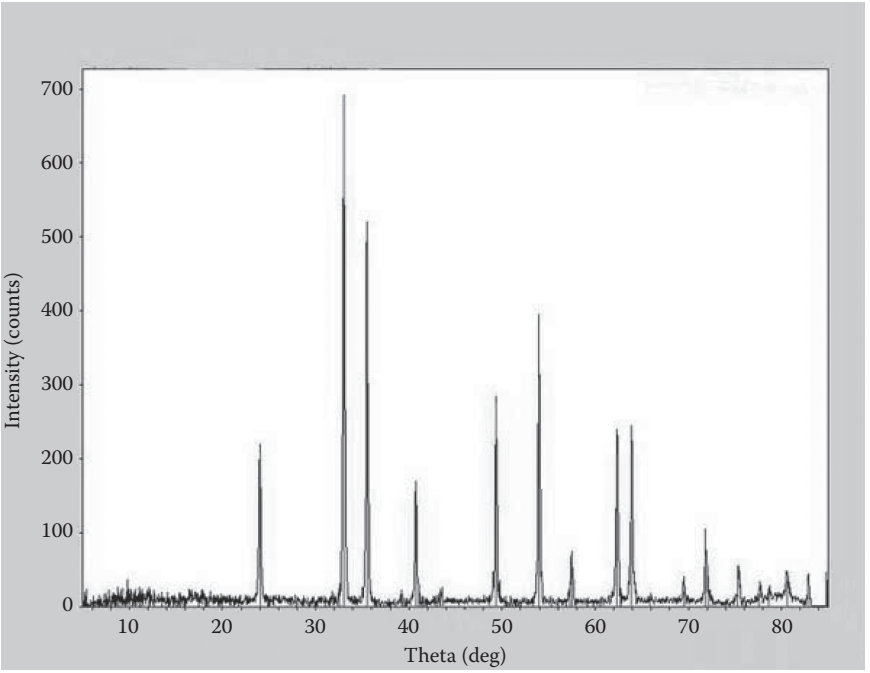


FIGURE 21.13 Crystalline, low-background WAXD pattern of calcium sulfate.

on carbon, or even an organic salt of Ca. WAXD of deposits, removed either from a heat exchanger or an RO membrane or on filters collected during precipitation experiments, provides crystalline phase information about those materials.

The theory of WAXD is based on the interactions of x-rays with the crystalline planes in materials. The resulting pattern takes the form of peaks of varying intensities with the x-axis measured in either analysis angles (degrees 2-theta) or d-spacing (Å) and the y-axis measured in counts per second. A typical crystalline low-background WAXD pattern for $CaSO_4 \cdot 2H_2O$ is shown in Figure 21.13, and a typical noncrystalline, mostly amorphous, pattern is shown in Figure 21.14 for silica. A crystalline WAXD pattern as illustrated in Figure 21.13 typically allows the analyst to obtain a rather unambiguous identification of phase(s) using search-match programs with a high degree of certainty, given the pattern's well-formed reflections, excellent resolution, and low background. On the other hand, an amorphous pattern such as that illustrated in Figure 22.14 makes phase identification nearly impossible; the best that can be achieved on this type of pattern is to determine the d-spacing of the approximate centroids of the broad reflections and to combine the EDS information with the d-spacings to manually search for sensible matches. The broad reflections can also be caused by very small (sub-micrometer) PS; in this case, the material was the ~200 nm SiO_2.

Current WAXD acquisition is entirely computer-based and essentially automated. The sample preparation is the most labor-intensive portion of the analysis; if working with freestanding particles, they must be placed in the sample holder in a way that

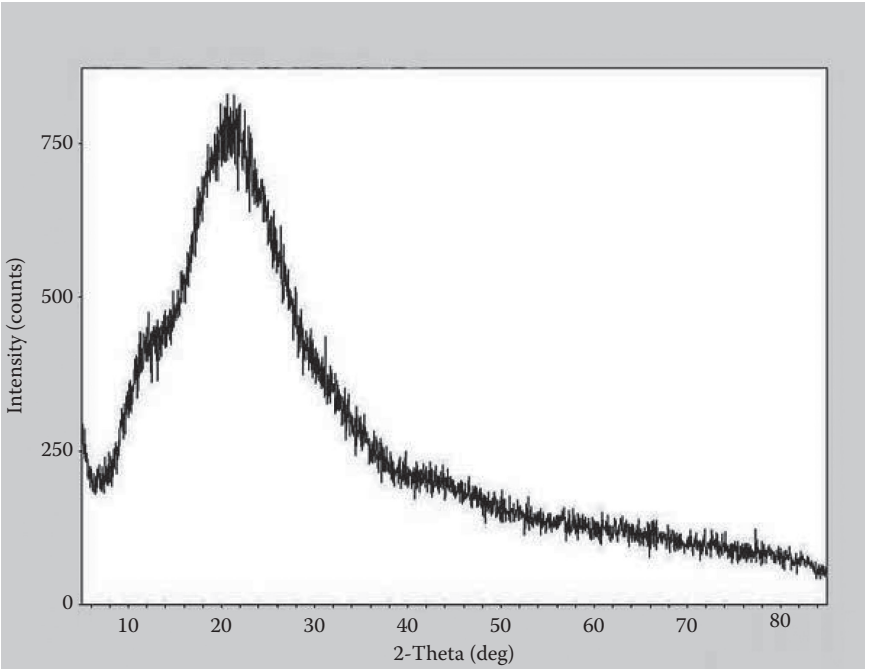


FIGURE 21.14 Mostly amorphous, high-background WAXD pattern of silica.

does not impart preferential orientation, and if working with particles on filters, the filters must be mounted in or on a holder in a way that does not change the sample height with respect to the incident x-rays. Preferred orientation can change a pattern such that it may not match known references, and sample height above or below the incident beam level of the sample holder can lead to 2-theta shifts in reflection positions. Both of these pattern changes can confuse the computer-based interpretation of the patterns and must be considered.

WAXD application programs are also completely computer driven, and their operations range from basic marking of reflections to full quantitative analysis. Phase identification can be performed manually or automatically. Manual identification requires a general idea of phases that may be present in a material and the use of commercially available databases that one can search by chemistry, strongest reflections, phase name, etc. Once reasonable candidates are identified, they can be visually applied to a pattern to check for fit. Automatic phase identification also uses the databases, but allows the analyst to tailor the searches for chemistry, statistical fit, preferred orientation, and many other aspects.

One of the more common applications of WAXD in the study of mineral scales and deposits is the determination of the polymorphs of $CaCO_3$. The polymorphs of most interest are the calcite, vaterite, and aragonite forms of the calcium carbonate. These forms have distinct WAXD patterns whose strongest reflections are well resolved from each other. Figure 21.15 illustrates a typical WAXD pattern of $CaCO_3$ with the different polymorphs indicated.

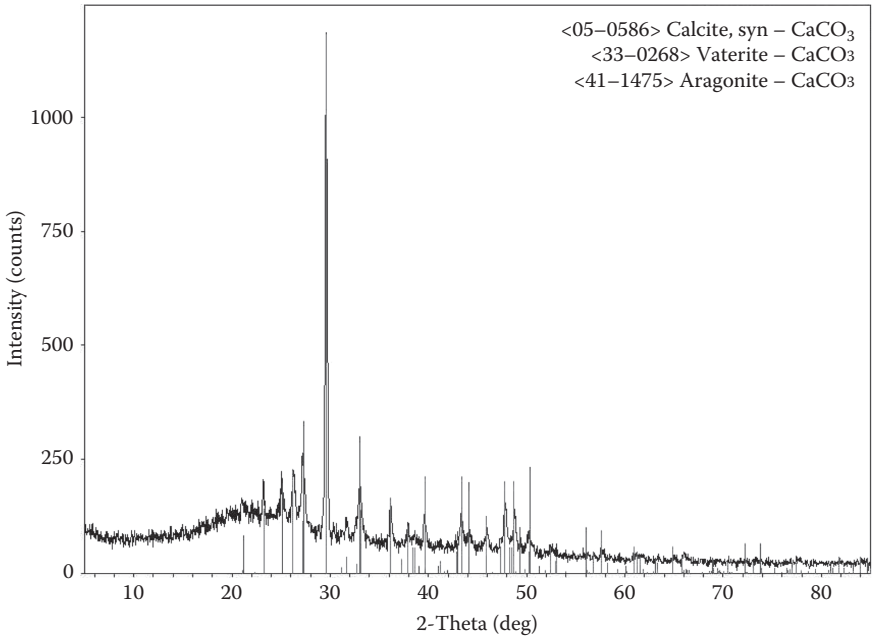


FIGURE 21.15 Well-resolved WAXD pattern of a mixture of calcium carbonate polymorphs—calcite, vaterite, and aragonite.

If deposits are directly on filters, it is important to acquire a reference pattern of an unadulterated filter under identical conditions to the deposits. The reference filter pattern can be used for qualitative comparison to (via overlays) or quantitative subtraction from the analysis patterns. A type of semiquantitative analysis of crystalline patterns can be accomplished if the phase identification is robust, the strongest reflections for those phases are well resolved from each other, and the background can be reasonably removed. For each element in the periodic table, mass absorption coefficients for various x-ray sources have been determined and are available in various reference tables. To determine the mass absorption coefficient of a compound, the elemental fractional composition of the compound is determined, each fraction is multiplied by the mass absorption coefficient for that particular element, and those products are summed to obtain the compound coefficient. The exercise for determining the mass absorption coefficient for $CaCO_3$ using Cu K-α radiation is illustrated as follows:

1. Determine the wt. fraction (f) of elements in $CaCO_3$:
   a. MW $(CaCO_3) \cong 100$ (1 mol Ca × 40 g/mol) + (1 mol C × 12 g/mol) + 3 mol O × 16 g/mol)
   b. Wt. fraction Ca ≅ 40/100 = 0.40
   c. Wt. fraction C ≅ 12/100 = 0.12
   d. Wt. fraction O ≅ 28/100 = 0.48

TABLE 21.2
Mass Absorption Coefficient μ/ρ Calculation for Compound $CaCO_3$

Element	Wt. Fraction (f)	μ/ρ	f × μ/ρ
Ca	0.40	162	64.80
C	0.12	4.60	0.55
O	0.48	11.5	5.52
Compound			
$CaCO_3$			70.87

2. Mass absorption coefficients μ/ρ for elements Ca K-α (X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials [4])
   a. μ/ρ Ca = 162
   b. μ/ρ C = 4.60
   c. μ/ρ O = 11.5
3. Mass absorption coefficient μ/ρ for compound $CaCO_3$ is shown in Table 21.2.

Once the mass absorption coefficients are determined for the compounds of interest, the next step in the semiquantitative analysis is to determine the net (background-subtracted) counts in the strongest reflections for each compound. The modeling of backgrounds and their subsequent subtraction and determination of the net counts are reasonably facile procedures in current WAXD analysis programs. Then, the net counts for each compound are multiplied by the mass absorption coefficient for the compounds, and those products are summed. Finally, the individual products are divided by the sum, and compositional fractions are obtained, as illustrated in Table 21.3 for a well-resolved, robust mix of $CaCO_3$, $CaSO_4$, and CaO. If the pattern consists of polymorphs of the same compound, there is no need to incorporate the mass absorption coefficients as they will be the same for each polymorph.

TABLE 21.3
Determination of Approximate Phase Composition in a WAXD Pattern Using Net Areas under the 100% Reflections and Compound Mass Absorption Coefficients

Compound	μ/ρ (Rounded)	Net Counts	μ/ρ* Net Counts	~Fraction Compound
$CaCO_3$	71	15,000	1,065,000	0.3
$CaSO_4$	74	24,000	1,776,000	0.5
CaO	118	6,200	731,600	0.2
			3,572,600 (total)	

In that case, a simple determination of the fractions based only on the net counts in the strongest reflection for each polymorph is indicated.

21.3 PARTICLE SIZE ANALYSIS

For particles deposited on filters or substrates, SEM or reflected light optical microscopy can be used to obtain various size measurements, including average size and size distribution. For suspensions of particles (i.e., calcium carbonate, iron oxide, clay, in aqueous medium), automated particle analyzers are commonly used to provide many types of particle information. Modern analyzers are of several types, including x-ray sedimentation, electrical sensing zone, and laser light scattering. The PS ranges and the analytical basis for each method are listed in Table 21.4 [5].

Figure 21.16 illustrates the typical output from a laser light scattering instrument, with particle diameter on the x-axis and volume % on the y-axis. Figure 21.17 presents an excellent example of PS distribution of iron oxide in the absence and presence of a polymeric dispersant. As may be seen, the presence of 1 mg/L of Carbosperse™ K-781 exhibits a significant effect on the PS distribution and causes a reduction of larger particles to smaller-size particles. This type of information is useful in benchmarking dispersants of different polymer architectures.

TABLE 21.4
PS Analysis Ranges for Three Most Common Techniques

Technique	PS Range (μm)	Theory
X-ray sedimentation	0.1–300	Natural size separation upon settling; mass fractions sensed by soft x-ray absorption
Electrical sensing zone	0.5–1000	Electrical signal proportional to volume of particles swept through an orifice; counts particles and determines concentration
Laser light scattering	0.02–2000	Mie's and Fraunhofer's theories to determine PS distribution from a light scattering pattern

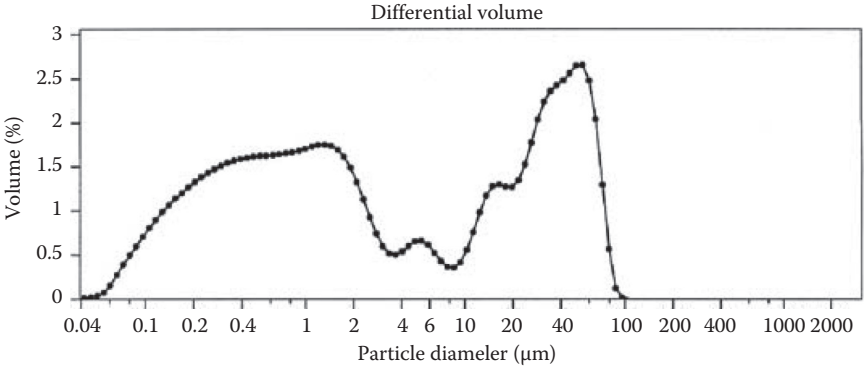


FIGURE 21.16 Typical output from laser light scattering PS analyzer.

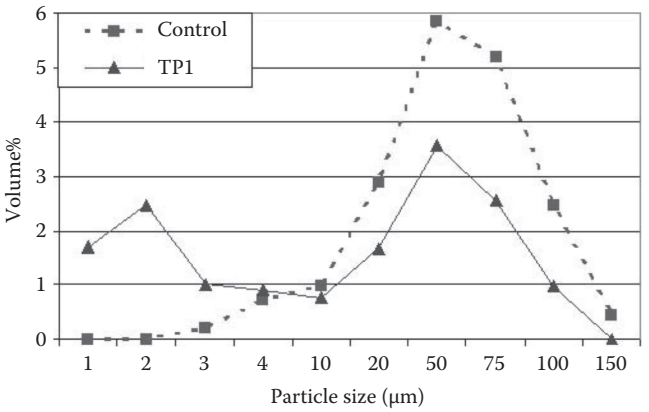


FIGURE 21.17 Comparison of PS distributions of iron oxide in the absence and presence of a polymeric dispersant.

21.4 OTHER ANALYTICAL TECHNIQUES

Inductively coupled plasma (ICP) analysis is a wet-chemical method for the quantitative determination of most metallic elements from the percent level to parts per trillion (ng/L). The method requires that the sample can be taken up in a solution (some samples may require ashing and/or acid digestion) so that it can be aspirated into a plasma. The resulting atomic vapor emits light that is detected; the wavelengths are element specific so that their intensities are proportional to the amount of analyte in the liquid sample. The method requires analysis of standard concentrations of the analytes in matrix-matched solutions to determine the response of the detection system. This method is particularly helpful when it is necessary to determine very low concentrations of metals in solutions from water treatments.

X-ray photoelectron spectroscopy (XPS) (or colloquially electron spectroscopy for chemical analysis, [ESCA]) is a surface-sensitive elemental analysis technique. Electrons are ejected from inner or outer shells when excited by x-rays (the converse of EDS analysis, whence electron excitation causes ejection of x-rays). Each element has a specific binding energy that is affected by its atomic number and its coordination with other atoms. The position of the resulting peaks and their shifts from literature values aid the analyst in determining what analytes are present and if (and how) they are bonded to other atoms. XPS is sensitive to the first 10–50 Å of a surface and is particularly valuable when analyzing thin deposits of films of materials on substrates.

21.5 SUMMARY

A variety of analytical techniques are available to analyze complex mineral scales and deposits commonly encountered in industrial water systems. In selecting a method of analysis, the important roles played by various microscopic methods, EDS, and WAXD, in identifying composition, crystalline structure, and crystal morphology

of foulants, should be considered. The utility of PS analysis in studying changes in the PS of foulants such as iron oxide, clay, and calcium carbonate (especially in the presence of deposit control polymers) must also be kept in mind.

REFERENCES

1. Amjad, Z., *Reverse Osmosis: Membrane Technology, Water Chemistry, and Applications*, Van Nostrand Reinhold, New York (1993).
2. Schroeder, C. D., *Solutions to Boiler and Cooling Water Problems*, The Fairmont Press, Inc., Atlanta, GA (1986).
3. Cowan, J. C. and Weintritt, D. J. *Water-Formed Scale Deposits*, Gulf Publishing Company, Houston, TX (1976).
4. Klug, H. P. and Alexander L. E. *X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd edn., John Wiley and Sons, Inc., New York (1974).
5. http://www.particletesting.com/particle_size.aspx, Micromeritics Analytical Services, Norcross, GA (2008).