CHAPTER 7: ECONOMIC GEOLOGY

Economic Aspcts of Shales and Clays: An Overview

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Introduction

Since 1908, when Sorby remarked on the intricacies involved in the study of muds, considerable advances have been made in furthering our understanding of mudstones and shales. Indeed, today's novice student in the field of shale research will speedily find him/herself reviewing models pertaining to a variety of rather sophisticated processes dealing with shale deposition and accumulation. These include questions concerning the modern environments of mud deposition, diagenetic changes and the transformation of muds to mudstones and shales, the significance of preserved biogeochemical signatures, syngenetic and epigenetic mineral deposits, weathering products, and the role of shales as hydrocarbon source rocks.

Preceding chapters in this volume have dealt with our growing understanding of mudstones and shales with regard to sequence stratigraphy, basin analysis, depositional processes and shale facies, petrography and petrology, inorganic and organic geochemistry. One aspect, however, the economic importance of mudstones and shales and of their constituent minerals, predominantly - clays, has often been neglected in other treatments of the subject.

The purpose of this overview, therefore, is to present a brief synthesis of information pertaining to the many uses of shales and clays. We hope that the following treatment of the topic will prompt future shale researchers to: 1) recognize the versatility of shales and clays in terms of current uses, and equally important 2) to explore new avenues of research whereby additional uses for shales and clays may be discovered and developed. Although we do not intend to cover all of the studies pertaining to the economic uses of shales and clays, we hope to have provided an adequate overview of the diverse applications of shales and clays and helped to identify research directions for future work.

General characteristics

Mineralogically, typical muds are characterized by approximately 50% clay minerals, 30% quartz, and 10% each of feldspars and carbonate-iron oxide cements (Boggs, 1992). Raymond (1995) synthesized mineralogical data from a variety of mudrocks and illustrated the importance of accessory mineral phases in shales and mudstones, such as zeolites, sulfates, sulfides, apatite and hornblende. Clays, or the phyllosilicate group of minerals, are mainly responsible for the physico-chemical properties exhibited by mudrocks. Although a large variety of clay minerals can be found in individual samples of a clay-rich sediment, the more common types are kaolinite, illite, chlorite, vermiculite, montmorillonites, and mixed-layer clays. For details of clay mineralogy and chemistry, the reader is referred to works by Grim, 1968; Millot, 1970; Velde, 1985; Chamley, 1989; Moore and Reynolds, 1989; and Raymond, 1995.

The original mineralogy of a mud deposit typically changes due to effects of lithification and post-burial diagenetic processes. In general, the clay fraction of mudrocks that are subjected to progressive burial undergo illitization (see Dunoyer de Segonzac, 1969; Singer and Müller, 1983; Frey, 1987; reviews by Chamley, 1989; Moore and Reynolds, 1989). Additional chemical interactions during progressive burial my lead to dolomitization of calcitic components, neoformation of zeolites as cements, authigenesis of kaolinite, and changes in crystallinity of clay species. The original mineralogy of a mudrock is primarily controlled by source lithologies, however, selective accumulation may also occur in specific environments of deposition (e.g. Windom et al., 1971). Detrital kaolinite, for example, has been found to preferentially accumulate in shallower, paralic settings as opposed to the other species (Edzwald and O'Melia, 1975; Gibbs, 1977; and references in Weaver, 1989).

While a number of workers have concerned themselves with investigations of shales and clays with a view toward reconstructing ancient sedimentary environments and conditions of burial diagenesis, a simultaneous effort has been undertaken to advance our knowledge of the tremendous variety of economic uses that shales and clays lend

themselves to. It is the latter endeavor, however, which has for the most part eluded the attention of the general public interested in a survey study of fine-grained sediments.

The following sections cover a variety of aspects of shales and clays, including their role (1) as source rocks for hydrocarbons, (2) as a host for metal deposits, (3) in the ceramics and manufacturing industry (pertaining to the production of a variety of products including but not limited to paper, rubber, pharmaceuticals, pesticides, paints, fiber glass, and processing of ores), (4) engineering geology applications, and (5) in disposal of medium- and high-level radioactive and hazardous waste.

Shales as Hydrocarbon Source Rocks

What makes a given sedimentary basin a hydrocarbon province has long been of interest to geologists. Because the origin of hydrocarbon source rocks and the factors that are responsible for enhanced preservation of organic matter are most likely revealed through studies of rocks rich in organic matter, black shales have been the focus of this inquiry (e.g., Miller, 1980; Arthur et al., 1984; Demaison, 1991; Calvert, 1987; Calvert and Pederson, 1992; Arthur and Sageman, 1994; Wignall, 1994). For a long time, it was widely believed that generation of source rocks was primarily due to depletion of benthic dissolved oxygen and a resulting lack of aerobic decomposition of organic matter in surface sediments. This postulated linkage between bottom water anoxia and organic matter preservation, however, has been questioned in recent years. Studies of modern marine environments suggest that assumption of such a direct relationship is overly simplistic, and that productivity of surface waters is equally important (Calvert, 1987; Pederson and Calvert, 1990; Calvert and Pederson, 1992; Pederson et al, 1992; Arthur and Sageman, 1994). No matter how the productivity versus preservation debate will be resolved through future research, the fact remains that enormous quantities of hydrocarbons have originated in carbonaceous shales and mudstones (Townes, 1993; Gautier et al., 1996).

In the past two decades petroleum has been by far the largest source of energy for humanity (~310 quadrillion Btu), followed by coal, gas, hydroelectricity, and nuclear energy (Townes, 1993). Unfortunately, hydrocarbons represent a finite resource that is rapidly drawing closer to depletion. In fact, discounting the 750 Billion Bbl already depleted, the world has currently available only 1,000 Billion Bbl as proven reserves, and an additional estimated 1,000 Billion Bbl of undiscovered resources (Townes, 1993). Even with an optimistic scenario of an ultimate recovery volume of 3,000 Billion Bbl, all hydrocarbon resources will be exhausted by the year 2250 AD (Townes, 1993; Gautier et al., 1996). The task ahead, for explorationists, is the efficient targeting and recovery of the 1,000 Billion Bbl of the hitherto undiscovered resource. How effectively this task will be accomplished may well hinge on progress in some key areas of stratigraphic and sedimentologic research, especially as pertaining to fine-grained sequences. Future research must target the fine-grained source rocks (Posamentier and Weimer, 1993), with special emphasis on integrating their sequence stratigraphic character with petroleum systems concepts (sensu Magoon, 1988; Demaison and Huizinga, 1991), in order to optimize exploration success in such facies. Likewise, although original chemical compositions and later diagenetic transformations of fine-grained strata have received much attention (e.g. with regard to the origin of cherts and phosphorites), much work remains to be done to improve our understanding of the occurrence of such strata within a sequence stratigraphic framework (Schwalbach and Bohacs, 1992).

In light of dwindling hydrocarbon resources, increasing attention is being paid to the prospect of developing oil-shales as an alternative source. Over geologic time, oil shales have accumulated in a variety of depositional settings (Yen and Chilingarian, 1976; O'Brien and Slatt, 1990). In the United States alone, oil shale resources are estimated to exceed 2,000 Billion Bbl of petroleum (at 42 U.S. gallons, or 159 liters, per barrel); about 130 times the known U.S. reserves of petroleum (Russell, 1990).

The proven oil-shale resources of the world approximate 5.1 trillion barrels of oil (Bachman, 1993). Of these, the largest single oil-shale accumulation is found in the U.S., in an area covering approximately 42,700 km^2 (16,500 square miles) in parts of Colorado, Utah, and Wyoming (Russell, 1990). These sediments are widely known as the Green River Formation (Russell, 1990) and accumulated in two large Eocene lakes. Within the Green River Formation, the largest deposits of high-grade oil-shale occur in the Piceance Basin of northern Colorado. About 1,000 feet of oil shale is present beneath 500-1,600 feet of sandstone and lean shales and is estimated to contain an equivalent of ~ 1.3 trillion barrels of oil (Bachman, 1993). Large deposits of Late Devonian and Early Mississippian oil shales occur in parts of Indiana, Kentucky, and Tennessee (Russell, 1990), and are known under names such as Chattanooga Shale, New Albany Shale, and Ohio Shale. The better explored portions of these deposits are estimated to contain ~ 200 Billion barrels of oil, and areas which are less well known may contain an additional 800 Billion barrels. The oil yield from these shales is 10 gallons or more per ton (Russell, 1990). Diatomite-rich petroliferous shales of Miocene age abound in southern California and contain approximately 70 billion barrels of oil (Gautier et

al., 1996). Presently, only shales with a yield capacity of 25-65 gallons per ton have been commercially exploited. Technological advances, however, may in the future allow economic utilization of occurrences with oil yields as low as 10 gallons per ton (Russell, 1990). The economics of mining may also be improved by extraction of certain metals (e.g. U, V, Mo, etc.) that are enriched in carbonaceous shales (Bachman, 1993; see also contribution by Leventhal to this chapter).

Brazil contains a major oil-shale interval, the Irati trend, that extends from the state of Sao Paulo to the Uruguayan border. The deposit of Sao Mateus de Sul, which covers ~ 32 square miles has semiproven reserves approaching 630 million barrels of oil. The African and Asian continents are estimated to contain between 100-75 billion barrels each (Bachman, 1993). A comprehensive compilation of world wide oil shale occurrences and resources is provided by Russell (1990).

Another potential benefit of oil shale is the utilization of solid waste produced during oil shale processing. Such waste materials can include retorted oil shale, raw shale fines, spent catalysts, elemental sulfur, and biological treatment sludges. Decarbonized western oil shales (retorted Green River oil shale) exhibit a remarkable capacity to cement, and may be useful as a low grade cement substitute. Raw shale rejects and fines from mining and raw shale preparation could be processed into bricks and briquettes. Spent catalysts could potentially be reclaimed and reused. Elemental sulfur reclaimed from air pollution control scrubbers could be utilized in agriculture. Specialty chemicals may become another economic spin-off from the oil shale industry. Complex oil shale components with high molecular weights, low pour-point resin properties, and high concentrations of different functional groups could see use in production of waxes, asphalt, lubricating oils, sulfaonate feeds, and resins (Russell, 1990).

Caution, however, needs to be exercised in our efforts to utilize oil shales on a massive scale. This need stems from the fact that a future boom in the oil shale industry will no doubt, be accompanied by large volumes of solid waste products mostly consisting of retorted oil shales, raw oil shale fines, overburden and subgrade shale ore, codisposed water, and other smaller amounts of hazardous wastes. The solid wastes could potentially produce leachates that may contaminate the groundwater, in addition to threats posed by potential mass failure or autoignition of waste dumps. Future research must address these safety issues.

Ore Deposits in Shales

Shales, especially those that contain appreciable quantities of organic carbon, have long been known to be enriched with a variety of transition metals, especially Mo, Zn, Ni, Cu, Cr, V, Co, Pb, U, and Ag (Vine and Tourtelot, 1970). Careful petrographic studies typically reveal a variety of metal sulfides in shales, and suggest that sulfide minerals are an integral part of sediment diagenesis (e.g. Ramdohr, 1953; Schneiderhöhn, 1955; Mempel, 1962; Mossler, 1971; Amstutz and Park, 1971; Vulimiri and Cheney, 1980; Hofmann, 1989; Schieber, 1991). A useful overview of sedimentary ore deposits that also contains information and references about shale-hosted ores is the book by Maynard (1983).

Metal-rich black shales are the most common type of shale hosted metal concentrations. They typically require conditions that are conducive to accumulation of large quantities of organic matter and slow accumulation rates so as not to dilute the accumulating metals. Metals are typically derived from seawater, either directly or via pre-concentration in planktonic organisms. Unusual circulation patters and volcanic ash deposition may enhance metal enrichments. A detailed discussion of metal-rich black shales and pertinent references can be found in the contribution by Leventhal to this chapter.

Aside of these wide-spread, but low-grade metal deposits, shales are also host to some of the worlds largest economic deposits of copper, lead, and zinc. Of these, the Kupferschiefer of central Europe is probably one of the most widely known occurrences. Mined since the Middle-ages (Schneiderhöhn, 1921), Kupferschiefer mining continued in Germany until very recently (e.g. Jung and Knitschke, 1976), and still continues in Poland today (Oszczepalski, 1989). Although generally very thin, the Upper Permian Kuperschiefer is a transgressive black shale deposit that extends from Poland to Britain and covers an area in excess of $600,000$ km^2. Low-level syngenetic base metal mineralization is ubiquitous in the Kupferschiefer, but metals were also derived from underlying sediments and fixed via bacteriogenic sulfate reduction, introduced by oxidative metal-rich brines during late diagenesis, and deposited epigenetically by hydrothermal solutions along structural features (Vaughan et al., 1989). Ore tonnages estimated for individual ore fields in the Kupferschiefer range from 75×10^6 metric tons to more than 1000×10^6 metric tons with base metal contents (Cu, Pb, Zn, Ag) of 2 to 5 percent (Gustavson and Williams, 1981). The Upper Permian Creta copper shales in Texas have been considered a possible North American analog to the Kuperschiefer (Huyck and Chorey, 1991), but in terms of depositional environment the two occurrences differ. Whereas the Kupferschiefer is generally considered the deposit of an epicontinental sea (e.g. Vaughan et al., 1989), the copper shales at Creta appear to have accumulated in a sabkha setting (Smith, 1976).

Major base metal deposits in shales also occur in the Proterozoic of Australia, North America, and Africa. In Africa, the most significant and best known are the deposits of the Zambian Copper Belt. There, a series of stratiform copper-cobalt deposits is located in a 120 km belt of ore shale (Fleischer et al., 1976) that prior to mining contained at least $30x10^6$ metric tons of metallic copper (or 10^9 metric tons of ore at 3% copper; cobalt content 0.1-0.3%). Detailed summary descriptions of the various types of Zambian copper shale deposits can be found in a review article by Fleischer et al. (1976). Just like in the case of the Kupferschiefer, proposed modes of origin range from syndepositional to epigenetic (Fleischer et al., 1976), but a good case can be made that a substantial portion of the mineralization is syngenetic or early diagenetic (Fleischer et al., 1976; Garlick, 1981).

The Proterozoic of Australia contains several large and well known shale hosted Pb-Zn-Ag deposits, such as Mt. Isa, Hilton, McArthur River, and Lady Loretta (Gustavson and Williams, 1981). These deposits contain between $9x10^6$ to $240x10^6$ metric tons of ore with base metal contents ranging from 13 to 25 percent (Gustavson and Williams, 1981). The host shales are finely laminated, carbonaceous, and dolomitic, and appear to have accumulated in comparatively shallow water. The base metal sulfides form conformable laminae and bands within the host shale, and the various features of these deposits are consistent with sulfide-exhalative mineralization (e.g. Lambert, 1983).

In North America, well known shale hosted mineral deposits of Proterozoic age include the White Pine copper deposit in Michigan and the Sullivan Pb-Zn deposit in British Columbia. The White Pine copper deposit occurs in the Proterozoic Nonesuch Shale which has been interpreted as a lacustrine deposit within the Keweenawan Rift (Gustavson and Williams, 1981). In contrast to the African and Australian examples mentioned above, the White Pine mineralization is considered post-depositional. The recognition that on a regional scale the copper mineralization was discordant to bedding, and textural features that suggest replacement of early diagenetic pyrite by copper minerals, led to the proposal of a paleohydrological mineralization model by White (1971). White (1971) suggests that cupriferous formation waters were introduced into the Nonesuch Shale some time after deposition (but prior to lithification), and that copper mineralization was a result of pyrite replacement along a reaction front that moved through the sediments. The abundant sandstone and siltstone interbeds in the Nonesuch (Elmore et al., 1989) were probably essential for allowing large quantities of mineralizing fluids to move through the Nonesuch Shale. Although the White Pine deposit is rather large ($550x10^6$ metric tons of ore), it is considered a marginal deposit (Gustavson and Williams, 1981) because of its comparatively low ore grade (1.2 % copper).

The Sullivan Pb-Zn-Ag deposit of British Columbia occurs in deep water clastics of the Belt-Purcell basin. A lens-shaped ore body ($155x10^6$ metric tons of ore; average combined base metal content 12-13%) has been emplaced within a sequence of laminated carbonaceous shales and siltstones (Gustavson and Williams, 1981). Perfectly conformable, discrete layers and laminae of base metal sulfides alternate with barren shale/siltstone intervals. An altered breccia pipe is situated beneath the deposit and is considered the conduit for mineralizing fluids that were exhaled on the sea floor and deposited conformable layers of base metal sulfides (Lambert, 1983).

Sedimentary-exhalative deposits (sedex) like Sullivan, Mt. Isa, Hilton, McArthur River, and Lady Loretta are not exclusive to Proterozoic shale sequences. Comparable deposits also occur in various Paleozoic black shale basins. The Silurian Zn-Pb deposits of Howards Pass in Canada are for example located in graptolite shales and contain in excess of $100x10^6$ metric tons of ore at 7.5% combined base metals (Gustavson and Williams, 1981). Devonian representatives are the well known Zn-Pb deposits of Rammelsberg and Meggen in Germany ($30x10^6$ to $60x10^6$ metric tons of ore; average combined base metal content 12-40%; Gustavson and Williams, 1981), and the Selwyn Basin Pb-Zn deposits in the Yukon territory of Canada (Carne, 1979; Gardner and Hutcheon, 1985). A major Mississippian deposit of this type is the Red Dog Zn-Pb deposit of Alaska (Lange et al., 1985), that contains in excess of $85x10^6$ metric tons of ore at a combined base metal content of 22%. One feature that sets these Paleozoic sedex deposits apart from most of their Proterozoic counterparts is the fact that they either contain variable proportions of bedded barite, or are closely associated with bedded barite deposits (Gustavson and Williams, 1981).

In some black shales significant enrichments of noble metals (Gold and Platinum Group Elements) have been observed that may constitute a future resource (Yermolayev, 1995). In the Kupferschiefer for example (Kucha, 1982), a thin interval shows striking enrichment with Au (up to 3000ppm), Pt (up to 370ppm), and Pd (up to 1000ppm). Kucha (1982) explained the enrichment as the result of autooxidation and desulfurization of organic matter, enhanced by the catalytic properties of Platinum Group Elements (PGE's), gamma radiation from U-enriched kerogens, and very small sedimentation rates. Lesser, but nonetheless intriguing, enrichments of PGE's have been reported from some Mo- and Ni-sulfide bearing black shales in China and Canada (Grauch et al., 1991). Lower Cambrian black shales in southern China contain up to several hundred ppb's each of PGE's and Au in strata deposited as individual, metal-rich sulfide layers, 2-15 cm thick. The ore also contains up to 7.1% Mo, 7% Ni, 2% Zn, and 2.5% As (Grauch et al., 1991). Similar Ni-rich sulfide layers occur in Middle Devonian black shales in the

Canadian Yukon. Metal contents reach 5.7% Ni, 1.2% Zn, 0.24% Mo, and up to 900 ppb Pd, 700 ppb Pt, 46 ppm Re, and 6 ppm Ag (Hulbert et al., 1990).

Use in Ceramics, Structural Products and in the Manufacturing Industry

Shales and mudstones also lend themselves to a variety of uses which basically draw upon their generally high contents of clay minerals. Ever since sun-dried bricks were fashioned and laid up into walls in the Tigris-Euphrates valley of ancient Mesopotamia 5,000 years ago, clays have been utilized for manufacture of a variety of products. Clay was used in the earlier days in the manufacture of writing tablets, roof tiles, tombstones, and other products needing a flat surface. With time, uses of clay proliferated with manufacture of sinks, washtubs, blackboards, and mantels.

In modern times, clays offer a valuable, multifaceted raw material with diverse uses in a variety of manufacturing industries. Their uses range from production of rigid impermeable complex clay composites (e.g.: heat resistant tiles, electric insulators and terminals, bricks, drain pipes, flue linings, terra cotta, and porcelain products) to the manufacture of vitro-ceram products composed of crystallized oxide and silicate materials with a near-zero thermal expansion. Clays have also been used extensively in the paint manufacture industry. Whereas the earliest commercial uses of clays in the paint industry involved their use as inert fillers, modern uses are multifaceted, and include for example the use of kaolinite of specific size categories to assist dispersion of pigments and to increase their hiding potential. Clays are also used in oil-based paints to render a certain amount of thixotropy so as to produce a non-drip behavior. Clays are also a vital ingredient in paper manufacturing, where they are used as fillers, or to enhance opacity and printability with ink; and to produce a smooth, glossy surface. As soil additives, clays can enhance retention of moisture and vital nutrients for plant growth, such as potassium, iron, and calcium.

Advances in instrumentation have led to an increasing use of analytical techniques for exploring and assessing economic use(s) of clay minerals. Examples of such techniques include but are not limited to - X-Ray diffraction, Differential Thermal Analysis, Thermogravimetric Analysis, Infra-red Absorption Spectroscopy, Mössbauer Spectroscopy, besides Optical and Electron Microscopy. A large variety of engineering techniques has been utilized to characterize the economic potential of clay minerals by means of parameters such as viscosity, yield stress, dilatancy, thixotropy, rheopexy, and plasticity. Worrall (1986) provides a detailed overview of the economic uses of the rheological properties of clays. Applications include filter-pressing for use in removal of clay-type impurities in fine coal; controlling the characteristics of a casting-slip via manipulation of the clays rheological properties; and determining the optimal balance between viscosity and thixotropy of clays used as drilling muds in the petroleum industry.

Although mineralogically, clays can be classified into at least ten distinct classes (Chamley, 1989); industrially, the clay minerals are categorized into six groups as per the USBM (United States Bureau of Mines) [Virta, 1994]. These classes are ball clay, bentonite, common clay and shale, fire clay, fuller's earth, and kaolin. They are described in the following section, along with their applications, production areas, and production figures for recent years.

1) Ball clay: Ball clays are an economically important raw material in the manufacture of ceramics. A plastic, white-firing clay, ball clay is sedimentary in origin (Virta, 1994). It is typically composed of variable amounts of disordered kaolinite with major impurities of quartz and illite mica, in addition to minor amounts of organic matter, and iron and titanium oxides. Also recognized as blue, black, and ivory clays, depending on their color (and chemical composition), ball clays are mostly used in the manufacture of ceramics, stoneware, and facing bricks. They are especially attractive in the manufacture of ceramics because they impart a high unfired strength to whitewares. To increase the hardness of ceramic products made from ball clays is an area of considerable concern, and future research will likely explore the role of added organic-matter to aid hardening (e.g. Worrall, 1986). Other than being used in whitewares, ball clays are also a key ingredient in the manufacture of pottery, floor and wall tiles, as fillers in animal feeds, and in sanitaryware. (1993 value: $ 41.89 per ton; U.S.; Virta, 1994).

Named after the manner in which these clays were originally mined (in balls or rounded scoops), the main deposits in the United States are in Florida, Alabama, Kentucky and New Jersey. They generally occur in proximity to coal seams, and are mostly Lower Eocene in age. Elsewhere, they are mined in the Devon and Dorset regions of Britain, southern Saskatchewan in Canada, the Witwatersrand deposit in South Africa, and the Westerwald deposit in Germany (Worrall, 1986).

2) Bentonite: Bentonites are predominantly composed of expandable montmorillonitic clays with sodium as the dominant exchangeable cation. Swelling type bentonites are characterized by high sodium contents and exhibit a volumetric expansion of up to 20 times on hydration. Non-swelling bentonites, on the other hand, are high in calcium.

Bentonites represent an important economic resource and are used in adhesives, animal feeds, ceramics, in recycling paper, in decolorizing mineral oils, vegetable oils, and animal oils, in pelletizing, and in waterproofing (Virta, 1994). More recently, bentonites have been increasingly employed as a grouting material for the sealing of wells (Regele et al., 1993a; 1993b; 1993c; Wheaton et al., 1993). Wheaton et al., (1994), for example report on the results of a study designed to test several bentonite and Portland-cement-based materials for effectiveness as sealing materials for abandoned wells and seismic shot holes. Bentonites were found to be more efficient for use in sealing wells in seismically active areas because they tend to re-establish a seal after a disruption occurs. Certain questions, however, remain to be answered; among them the question of long-term stability of the bentonite-grout mixture. Chemically, bentonite grouts react with both the formation water and the host rock (Grim, 1968). Future research must be directed towards a more comprehensive examination of the long-term physico-chemical stability of grouts and towards the suitability of different sealant materials for use in specific host rock/formation water environments.

Bentonites are also used in pelletization of iron ores, in foundry sands (steel, iron, and nonferrous casting purposes), and in drilling muds. A more recent use has been in the manufacture of pet waste absorbents, accounting for 11% of the total bentonite production in 1993. (1993 value: $34.12 for swelling and $48.51 for non-swelling bentonite per ton; U.S.; Virta, 1994).

In recent years bentonites have also found use in water purification. Murcott and Harleman (1996) conducted a series of experiments aimed at testing the efficiency of chitosan/bentonite mixtures as coagulants and settling media for removing particulates from Lake Michigan water in Chicago's south water purification plant. Results supported the use of a chitosan/bentonite chemical coagulant regime for the removal of water particulates from the lake water.

Disposal of intermediate-level and high-level hazardous and radioactive waste is yet another area for bentonite application (e.g., Dixon et al., 1992; Felix et al., 1996). This particular use of bentonite is dealt with in detail in a separate section.

Predominantly as an alteration product of Cretaceous volcanic ash, bentonites of a commercial quality are mined in parts of Wyoming, South Dakota, Nevada and Mississippi within the United States. They are also mined in the Manitoba, Saskatchewan and Alberta regions of Canada. Significant deposits have also been exploited in the New South Wales and Queensland regions of Australia (Virta, 1994).

3) Common clay: Common clay is defined as a clay or clay-like material that is plastic enough to mold and has a vitrification point below 1,100 degree Celsius (Virta, 1994). Mostly composed of illite or chlorite, the common clays can also contain kaolin and montmorillonite. They are mostly used in the manufacture of heavy clay products including: building brick, flue linings, sewer pipe, drain tile, structural tile, terra cotta, and portland cement clinker. (1993 value: $ 5.41 per ton; U.S.; Virta, 1994).

4) Fire clay: Fire clays are often associated with coal measures, particularly the underclays situated beneath coal seams. Low concentrations of iron oxide, lime, magnesia, and alkalies in this clay allow it to resist temperatures of 1,500 degree Celsius and higher (Virta, 1994), thus the name. Often a by-product of coal mining, fire clays are used extensively in the manufacture of commercial refractory materials, including firebricks and blocks, grogs and calcines, saggers, refractory mortars and mixes, as well as in the production of lightweight aggregates, portland cement, bricks, and pottery (Worrall, 1986). (1993 value: $ 25.13 per ton; U.S.; Virta, 1994).

Important deposits are located in the Limburg, Westerwald, and Pfalz regions of Germany, the Forth-Clyde region of Scotland, the Lancashire coalfields of Britain, and the Normandy region of France. In the United States, well known deposits occur in Ohio, Pennsylvania, and Kentucky (Virta, 1994).

5) Fuller's earth: The term Fuller's earth does not refer to a clay with a specific composition, but is defined as a nonplastic clay or clay-like material, with a high content of magnesia. It was originally used for cleaning wool (fulling) and is suitable for decolorizing mineral and vegetable oils (Virta, 1994). Commonly composed of lath-shaped attapulgite or varieties of montmorillonite, it can also consist of opal and colloidal silica. Fuller's earth possesses a relatively large surface area, and high CEC (cation exchange capacity) and adsorptive capacity. Major uses of the attapulgite and montmorillonite types of Fuller's earth are in pet waste and oil and grease absorbents. The thixotropic properties of attapulgite clays render them attractive for use in manufacturing processes which require thickening and viscosity controls for suspending solids as in paint, compound cement, and saltwater drilling mud. In addition, Fuller's earth is also used in the refining of sugar solutions, pesticides, animal feed, syrups and wines, water and effluent treatment, foundry moulding sands, and as a plasticiser in ceramics (Worrall, 1986; Virta, 1994). The dominant use, however, is in pet waste absorbency (292,000 tons), accounting for over 60% of the total production in 1993 (1993 value: $ 125.75 per ton; U.S.; Virta, 1994).

6) Kaolin: Kaolin also known as china clay and is one of the economically most important clay types. A residual clay, it is typically composed of about 46% SiO_2 and 38% Al_2O_3; the rest being impurities consisting of

paragonite and muscovite with smaller amounts of iron, calcium, and magnesium oxide phases. Kaolin is especially valued for its color, the ability to impart a pristine whiteness to a product both in its raw and fired conditions. It is used in the manufacture of electrical porcelain, fiber glass, roofing granules, pharmaceuticals and cosmetics, pesticides, fine china and dinnerware, sanitaryware, adhesives, paint, plastic, rubber, foundry calcines, grogs, as fillers, coaters, and extenders in the paper manufacturing industry, and as an oil-refining catalyst (1993 value: $ 106.94 per ton; U.S.; Virta, 1994).

Within the United States, important deposits can be found along a 500-mile stretch that extends from Vermont to Georgia, and along the Mississippi valley. Georgia and Florida kaolins are characterized by especially low contents of iron and therefore find extensive use in manufacture of paper and ceramics (also see Worrall, 1986). Other significant deposits worldwide include the St. Austell kaolinite of Britain, the Echassieres deposit of central France, the Hirschaun deposit in Bavaria, Germany, the Quebec and northern Ontario deposits in Canada, and the Brakkloof and Norhoek deposits near Capetown, South Africa (Worrall, 1986).

Production statistics for the US

In 1993, a total of 330 companies operated 989 mines or clay pits in the U.S. (Virta, 1994). Clay production was conducted in all States and Puerto Rico except Alaska, Delaware, Hawaii, Rhode Island, Vermont, and Wisconsin. Most clay in the U.S. is extracted by open-pit methods (less than 1% was produced from underground mines in 1993). Readers are referred to Virta (1994) for a detailed breakdown of production figures for each of the individual types of economic clay classes. The different economic uses of clays can be summarized as follows: absorbent uses (Fuller's earth and bentonite), ceramics (ball clay, common clay and kaolin), construction (common clays used in expanded aggregates and structural clay materials), and hydraulic cement (common clays, kaolin, fuller's earth, fire clay and bentonite).

Given below are some of the production statistics associated with the major types of economically-useful clays in the US:

Structural clay products: Products include building brick, drain tile, flue linings, roofing tile, sewer pipe, and terra cotta. Common clay was most widely used for such applications. Slightly more than 12.3 million tons of common clay was utilized in 1993 in the US, with the building brick market valued at $ 985 million, and the market for floor and wall tiles amounting to a total of $ 678 million (Virta, 1994).

Drilling Mud: Clays are utilized to control the gel strength and viscosity of the drilling fluid and to coat the drill-hole walls to prevent loss of fluids. Swelling bentonites were the favored raw material in the industry with a demand of 559,000 tons in 1993 (Virta, 1994).

Filler: In 1993, more than 5 million tons of clay were used as extenders and fillers, with kaolin accounting for 82% of the total (Virta, 1994). Fuller's earth was used in fertilizers, pesticides, animal feed, paint, adhesives, and asphalt, whereas ball clay uses included wallboard, asphalt, tile, paper, and plastic. In 1993, approximately 947,000 tons of kaolin was used as paper filler (Virta, 1994).

Refractories: Ball clay, common clay, and fire clay were the most widely used clays for the manufacture of firebrick, bentonite for foundry sand, and kaolin for grogs and calcines (Virta, 1994).

Shales in Radioactive and Hazardous Waste Disposal

Another potentially important use of shales and mudstones is their application in the long-term (~10,000 years) containment and storage of intermediate and high-level radioactive wastes. Although the use of clay-rich rocks in this field is still in its developmental stages, there are numerous indications that shales and mudstones will be put to ever-increasing use as waste disposal sites. Options pertaining to waste disposal have been pursued for a variety of scenarios, such as above land, subsurface, and sub-sea. The North Pacific Deep-Sea Storage Project, for example, is an investigation of the feasibility of containment, packing, and disposal of high-level radioactive waste in the deep sea (Burkett et al., 1991). Other investigations have focused on underground storage, and have included feasibility studies of some well-known shales and mudstones, including the Pierre Shale, the Chattanooga Shale, the Green River Formation, the Nolichucky Shale, and the Pumpkin Valley Shale (Lomenick and Kasparowicz, 1991; Lee et al., 1991).

Although research concerning use of shales and clays in radioactive waste disposal has been ongoing for several decades now, at present we do not have a storage concept that will guarantee safe disposal over the required time span (~10, 000 years). Nevertheless, progress is being made and innovative ideas are currently being tested.

For example, the Canadian Nuclear Fuel Waste Management Program is evaluating a pilot project for geological storage of nuclear fuel waste at depths approaching 1000 m in the stable crystalline basement of the Canadian Shield (Dixon et al., 1992). In this particular project, use is being made of a bentonites ability to swell and

effectively seal a vault. Used fuel, stored in corrosion-resistant canisters will be emplaced either via in-room disposal (in rooms excavated in the rock) or borehole disposal (in holes drilled in the floor of the rooms) [see Dixon et al., 1992]. The canisters in turn will be surrounded by a buffer composed of equal dry-weight proportions of bentonite clay and graded silica sand, because bentonite will swell on contact with water and effectively prevent the through-flow of fluids. Bentonites also have the capacity to absorb certain radionuclides.

Some key questions, however, remain to be answered and will provide impetus for future research into this important application of clay minerals. They are as follows: 1) how well will the bentonitic buffer seal be able to withstand the heat and radioactive gamma radiation emanated by the waste? 2) how will chemically-treated bentonite-polymer complexes (with large, organic-chain molecules) withstand radiation over long periods of time? 3) will it be economically feasible to extract the desired quantities of a particular type of bentonite for use as a sealant?

Other examples of use of clay minerals in the field of radioactive waste disposal abound. Spanish scientists, for example, under the auspices of the European Atomic Energy Commission, have been evaluating the potential of utilizing illitic clay-crushed granite mixtures as barriers against migration of radionuclides via characterization of the mixtures physico-chemical properties and diffusion experiments in the laboratory (Mingaro et al., 1991).

An interesting method for permanent storage of solid radioactive waste was in operation at the Oak Ridge National Laboratory (ONRL) for almost 20 years (1970's-80's) [International Atomic Energy Agency, 1983]. This technique involved: 1) the mixing of radioactive waste effluents in a slurry containing grout, and 2) injection by fracturing into a deep, impervious (10^{-6} to 10^{-9} darcy) shale formation. The grout material chosen was of a specific composition so that it would solidify in the fractures along the bedding planes in the shale, thereby permanently isolating the radioactive waste from the surface. More recent progress in the application of such a technique for the disposal of radioactive waste, however, has not been published.

Other notable investigations concerning the feasibility of shales and mudstones as repositories for radioactive waste include those by Lee et al. (1991) [on the Pierre Shale, the Chattanooga Shale, and the Green River Formation shales]; Croff et al. (1986); Lee and Tank (1985); Lee et al. (1987); Stow and Croff (1987); and Lomenick and Kasprowicz (1991) [on the Huron shale, the Conasauga Group shales, the Pierre Shale, and the Green River oil shales].

Several studies have also focused on the more geotechnical aspects of shale use in radioactive waste repositories. Among the important questions that need to be addressed are the effects of waste on material consistency, material creep tendencies, hydraulic conductivity, compression strengths and cohesion properties of the rocks, permeability, and microfabric or grain-size changes (Meyer and Howard, 1983; Muller-Vonmoos et al., 1990; Nataraj, 1991; Burkett et al. 1991; Rhee, 1991; and Muller-Vonmoos et al., 1994). More recently, Felix et al. (1996) report the results of a long-term study conducted on the effectiveness of swelling clays as an engineered barrier material for disposal of radioactive waste in deep geological formations. They stress that future research must expand from laboratory characterization of clays to experiments where the thermo-hydro-mechanical behavior of clay-rich materials is examined in full-scale models involving storage and disposal in the field (Felix et al. 1996).

Shales in Engineering Geology

Although shales and mudstones are generally problematic materials to an engineering geologist, due mainly to their propensity for swelling and shrinking under varying moisture conditions (Mermut and Acton, 1985; Baker and Grabowska-Olszewska, 1995; Brattli and Broch, 1995) and also due to their quick-clay behavior (Lessard and Mitchell, 1985; Ohtsubo and Torrance, 1995); they also offer some positive engineering aspects. A common use is their application as aggregates and embankment filler materials (Otus and Sadigh, 1977). In West Virginia, for example, the Ordovician Martinsburg Shale and the Devonian Braillier Shale have both been used as lightweight (expanded) aggregate with uses in concrete, brick, asphalt, railroad ballast, road base and fill (Simard, 1990).

Clay Use in Landfill-Liner Systems

A relatively new use of clays which is likely to expand in the near future, is their application as nearly-impermeable liners in landfills (Needham, 1991; Murray et al., 1992). With time, every landfill generates potentially hazardous leachate and clay liners help contain the leachate within the landfill by forming a physical barrier. Because over time even the most rigorously-designed landfills are prone to failure, leaking leachate can represent a threat to groundwater sources (Lema et al., 1988; Ray and Chan, 1986; Borden and Yanoschak, 1990; Murray et al., 1992). Therefore increasing efforts are made to design liners as simultaneous reactive chemical systems with potential to trap (adsorb) large quantities of potentially toxic components contained within typical landfill leachate (Lun and Christensen, 1989; Majone et al., 1993; Holm and Zhu, 1994).

A number of workers have noted the excellent retaining properties of clay minerals vis-a-vis potentially harmful metals in the laboratory (Bourg and Schindler, 1978; Schindler and Stumm, 1987; Schindler et al., 1987; Van Bladel et al., 1993). Clay-rich soils have also been investigated with regard to their effectiveness in holding metals in the complexed state (Shuman, 1975; McBride, 1978; Christensen, 1983; 1989a, b). Experiments to use clays to extract metals (such as Pb, Cd, Be, Fe, Ni, and Zn) out of actual landfill-derived leachates have met with promising results (Artiola and Fuller, 1980; Christensen, 1989; Majone et al., 1993; Holm and Zhu, 1994).

No matter how attractive clay liner systems are from a chemical perspective, the design of landfills also has to take into account the physical attributes and limits of clay liners, in order to avoid containment failures. These physical attributes have been described by a number of authors and include liquid limits, plastic limits, plasticity index, grain-size distribution, porosity, permeability or hydraulic conductivity, shear strength and shrinkage potential (Hettiaratchi et al., 1988; Reades et al., 1989; Gordon et al., 1989; Manassero and Pasqualini, 1993; Wright, 1993).

Another aspect of clay liners which deserves more attention is the tendency of certain types of clay mixtures to develop micro- and macro-cracks in response to fluctuating moisture conditions; often leading to failure of the entire liner system (for example Wright, 1993). Further research is needed, to develop clay mineral composites (mixtures) which are crack-resistant over a wide range of ambient moisture regimes.

Slope failure in landfills is another liner-related topic. Seed et al., (1990) and Mitchell et al., (1990); provide detailed case studies of slope failure in a landfill due to sliding along three critical interfaces within the clay liner system (the HDPE (ethylene) geomembrane, the geotextile, the contact between geomembrane and saturated compacted clay). Obviously, more design research is necessary to prevent mishaps of that kind in the future.

Organic compounds in clay liners can also be an important factor in their overall mechanical and chemical performance. Several studies have been conducted to investigate complexation of organic compounds with metals derived from landfill leachates (Bourg et al., 1978; Davis and Leckie, 1978; Dalang et al., 1984; Davis, 1984; Castagnoli et al., 1990; Holm, 1990 and Gu et al., 1994), but our knowledge of these processes is still quite preliminary. Future advances in our knowledge of clay-humic composites may bring liners with a greatly enhanced ability to absorb potentially toxic metals and thus enable us to construct safer landfills.

Conclusion

With so many aspects of our modern life being touched directly or indirectly by products mined or extracted from shales and clays, by products manufactured from clays, and by processes that involve clays, there are obviously many good and practical reasons to learn more about shales and clays. Thus, as a discipline of scientific inquiry, the study of shales, mudstones, and clays will most likely see considerable growth in the future.

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