# SUPPLEMENTAL MINERAL REPORT COMMON VARIETY DETERMINATION

## KIRKLAND TUFF DEPOSIT, YAVAPAI COUNTY, ARIZONA CAPITAL ASSOCIATION PLACER MINING CLAIM AMC 367119

Section 28, T. 13 N., R. 4 W., Gila & Salt River Meridian, Yavapai County, Arizona

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1

| Summary  | 7  |
|--|----|
| Introduction   |    |
| Purpose  |    |
| Legal Framework                                      |    |
| Assignment   |    |
| Scope  |    |
| Land Status and Record Data                          |    |
| Physical Features and Access                         |    |
| Field Work, Sampling Procedures, and Analytical Work |    |
| Field Work   |    |
| Sampling   |    |
| Analytical Work                                      |    |
| Regional Geology and Mining History                  |    |
| Regional Geology                                     |    |
| Regional Mining History                              |    |
| Geology and Mineral Deposits                         |    |
| Geology  |    |
| Mineral Deposits                                     | 21 |
| Deposit characteristics                              |    |
| Deposit commodities                                  | 23 |
| Potential Commodities                                | 23 |
| Natural Pozzolan                                     |    |
| Cement - General                                     |    |
| Portland Cement Manufacture                          |    |
| Cement Chemistry                                     |    |

# Table of Contents

| Types of Portland Cement                              |    |
|---|----|
| Blended Cements                                       |    |
| Pozzolans and Supplementary Cementitious Materials    |    |
| Silica Fume   |    |
| Ground Granulated Blast Furnace Slag                  |    |
| Fly Ash   |    |
| Natural Pozzolan - Characteristics and Specifications |    |
| Testing and Analytical Work for Natural Pozzolans     |    |
| Kirkland Tuff Pozzolan Characteristics                | 44 |
| Mineral Exploration and Development Work              | 47 |
| Mining, Milling, and Related Operations               | 47 |
| Mining methods  | 47 |
| Processing methods                                    | 48 |
| Common Variety Determination                          | 49 |
| Potential Deposit Products                            | 49 |
| Deposit Comparison                                    | 49 |
| Descriptions of Other Deposits Generally              | 50 |
| Identification of Competing Deposits                  | 56 |
| Pozzolan Market Overview                              | 57 |
| Cement and Concrete Markets                           | 57 |
| Market Area   | 58 |
| Market Demand   | 60 |
| Market Entry  | 62 |
| Mining and Processing Costs                           | 64 |
| Price Comparison                                      | 65 |
| Cost Comparison                                       | 66 |
| Common Variety vs Uncommon Variety Opinion            | 67 |

| Conclusions   | 68  |
|---|-----|
| Recommendations   | 69  |
| References Cited  | 70  |
| Appendices  | 74  |
| Appendix A - Land Status Maps   | 75  |
| Appendix B - Mining Claim Reports   | 79  |
| Appendix C - Tabulated Sample Summary   |     |
| Appendix D - Photo Documentation of Samples   | 89  |
| 1. Ninyo & Moore Samples (Cortright and Abramson-Beck (2015))   | 90  |
| 2. Sandwell-Weiss Drill Hole Samples (Sandwell-Weiss, 2016)   | 95  |
| 3. Kirkland Samples - August 2016   |     |
| Appendix E - Chain Of Custody Documents   | 109 |
| Appendix F - Mineralogy and Chemical Analyses   | 122 |
| 1. Intertek Report - September 11, 2013   | 123 |
| 2. Arizona State University (ASU) XRD analysis excerpt (adopted from Kirkland file KMP_XRD_Plots.docx). | 131 |
| 3. The Mineral Lab March 29, 2016, Analyses   | 135 |
| 4. Hazen research April 26, 2016, report  | 147 |
| Appendix G - Chemical and Physical Test Data - Natural Pozzolans  | 180 |
| 1. Arizona State University (ASU) Analyses  | 181 |
| 2. Magmatics Analyses   | 185 |
| 3. CTL Thompson Analysis  | 190 |
| Appendix H - Other Deposit Data   | 192 |
| Naturalite mine - Nevada Cement   | 193 |
| Mustache Mine - Nevada Cement   | 195 |
| Rocky Mountain Mine - CR Minerals   | 197 |

| Wright Creek Mine - Hess Pumice  | 200                |
|--|--------------------|
| White Vulcan Mine - Formerly Arizona Tufflite  | 203                |
| Hazen Mine - EP Minerals   | 206                |
| Helmer-Bovill - I-Minerals   | 208                |
| Lassenite Mine - Geofortis   | 211                |
| Antelope Creek Quarry - Schuck Development   | 213                |
| Nevada-California Compilation  | 215                |
| igures   | 217                |
| Fig. 1. Location map of the Kirkland tuff deposit, Yavapai County, Arizona                                   | 218                |
| Fig. 2. Topographic and mining claim location map, Kirkland tuff deposit, Yavapai County                     | r, Arizona.<br>219 |
| Fig. 3. Air photo showing the Capital association placer mining claim (modified from Goog ,January 4, 2017). | gle Earth<br>220   |
| Fig. 4. Terrain and strata along the western side of the Capital MC.   | 221                |
| Fig. 5. Terrain and quarry in the west central Capital MC  | 222                |
| Fig. 6. Terrain and stockpile in west central part of the Capital MC.  | 223                |
| Fig. 7. Terrain and stockpile in the western and southwestern part of the Capital MC.                        | 224                |
| Fig. 8. Terrain across the quarry in the west central part of the Capital MC.                                | 225                |
| Fig. 9. Terrain and strata in the central and north central parts of the Capital MC                          | 226                |
| Fig. 10. Eastern claim line of the Capital Six lode mining claim in the central part of the Ca               | pital MC.          |
| Fig. 11. Historic stockpile in the western part of the Capital MC  |                    |
| Fig. 12. Terrain in the south central part of the Capital MC.  | 229                |
| Fig. 13. Outcrops and terrain in the southeastern part of the Capital MC                                     | 230                |
| Fig. 14. Outcrops and terrain in the southeastern part of the Capital MC                                     | 231                |
| Fig. 15. Outcrops and terrain in the eastern part of the Capital MC.   | 232                |
| Fig. 16. Physiographic map of Arizona showing the Kirkland tuff deposit location                             | 233                |

| Fig. 17. Regional geologic map of the Kirkland area  | 234        |
|--|------------|
| Fig. 18. Arizona industrial mineral deposits.  | 235        |
| Fig. 19. Geologic, sample distribution, and drill hole location map of the Capital MC.                     | 236        |
| Fig. 20. Type section of interbedded volcanic and volcaniclastic rocks in Sec. 33, T. 13 N., R. 4 W G&SRM. | 7.,<br>238 |
| Fig. 21. Indurated zone in the upper lithic tuff bed on the Capital MC                                     | 239        |
| Fig. 22. Flow diagram for the manufacture of cement  | 240        |
| Fig. 23. Example of common variety rock product prices, Phoenix, Arizona.                                  | 241        |
|  |            |

# List of Tables

| Table 1. Comparison of Kirkland tuff with average rock compositions                      | 23 |
|--|----|
| Table 2. Chemical shorthand and composition of clinker and portland cement               | 26 |
| Table 3. Typical mineralogical composition of modern portland cement                     | 28 |
| Table 4. Typical range in mineral composition and properties in types of portland        |    |
| cements  | 31 |
| Table 5. Typical range of fineness for the general types of portland cement              | 31 |
| Table 6. Physical and chemical properties of pozzolans and SCMs                          | 36 |
| Table 7. Natural and artificial pozzolans and SCMs classified by reactivity              | 36 |
| Table 8. Physical and chemical requirements for fly ash and natural pozzolans defined in |    |
| ASTM C618  | 39 |
| Table 9. Effects of pozzolans and SCMs on the performance of concrete                    | 42 |
| Table 10. Comparable deposit information   | 53 |
| Table 11. Salient statistics for cement in the United States                             | 57 |
| Table 12. Cement production in the U.S. by district                                      | 59 |
| Table 13. Proportion of raw materials used in the production of portland cement          | 61 |
|  |    |

#### Summary

Kirkland Mining Company (Kirkland) intends to file a mining plan of operations with the U.S. Bureau of Land Management (BLM) to develop its deposit on unpatented mining claims in sections 28 and 33, township 13 north, range 4 west, Gila and Salt River Meridian (Sec. 28 and 33, T. 13 N., R. 4 W., G&SR), Yavapai County, Arizona. The BLM regulations at Title 43, Code of Federal Regulations, Subpart 3809.101 (a) (abbreviated 43 CFR 3809.101 (a)) require that the BLM complete a mineral examination report to determine whether the subject mineral is locatable under the 1872 Mining Law, as amended, before it can process a mining plan of operations. This report was written to provide the BLM with supplemental information and an opinion whether the subject deposit is an uncommon variety and locatable under the mining law.

The Mining Law of 1872 (17 Stat. 91, 30 U.S.C. §§ 22 *et seq.*) provides that valuable mineral deposits can be embraced by citizens of the United States (U.S.) or U.S. companies through a process of location of mining claims. The original law applied to most mineral commodities. However, during the course of several decades, Congress amended the law to include only specific minerals and mineral substances. On July 23, 1955, Congress enacted the Common Varieties Act (also known as the Surface Resources Act of 1955; 30 U.S.C. §§ 611-615) which removed from location and operations of the mining law so called common varieties of minerals like sand, stone, gravel, pumice, pumicite, and cinders unless the deposit has some property giving it distinct and special value (30 U.S.C. § 611).

The BLM mineral examination report required by 43 CFR 3809.101 (a) would not address the efficacy of the mining claims. The required report is meant to address the question of whether the deposit at that location meets the criteria for an uncommon variety of mineral and is, thus, locatable. This report provides data and information to assist in the answer to that question and provides an opinion about the character of the deposit. This opinion is limited to the Capital association placer mining claim.

The Kirkland tuff deposit is located approximately 1.5 miles northeast of Kirkland, Arizona. The deposit lies in the central section basin part of the Arizona Transition Zone, a geomorphic province sandwiched between the Colorado Plateau province to the northeast and the Basin and Range province to the southwest. Mining claims have existed at the Kirkland tuff deposit site since 1896, and dimension stone to make facing and light weight block was most likely quarried from the site in those early days. Stone from the Kirkland site was used in the construction of the Arizona State Capitol building, probably at first construction in 1901 and definitely in the addition in the 1950s (Arizona Geological Survey, 2015, 1958 Engineers Report, Rynearson Kirkland Quarry file; Townsend, 1961, p. 29). Buildings in Congress and Yarnell also were constructed with the sawed stone from Kirkland in the early 1900s.

The Kirkland tuff deposit has been prospected since the late 1800s; however, no detailed geologic studies were conducted at the subject site until it was acquired by the Zouvas family. Cortright and Abramson-Beck (2015) conducted the most thorough recent work and mapped the lode mining claims on both the Capital and Homesteak MCs.

Since the geologic mapping, Kirkland has conducted further investigation through drilling and sampling and obtained analyses to determine whether the deposit can be mined and developed as a natural pozzolan. These data indicate that the Kirkland deposit is a



time to evaluate markets other than the natural pozzolan market. Thus, this report focuses on the higher value natural pozzolan commodity.

Background information is provided in this report to illustrate the complexity of cement chemistry and how the analytical data is used to determine the reactivity and performance of a natural pozzolan. Testing was completed in accordance with standard industry protocols as outline in ASTM C618, C311, C1527, and C1012. Results show the following.





Thus, the Kirkland tuff on the Capital MC has just the right intrinsic physical and chemical characteristics to allow it to compete among the elite of NP deposits. (b) (4)

For purposes of the common variety determination, the Kirkland tuff deposit can be compared with common variety deposits of materials used as aggregates for concrete and with other pumiceous deposit materials that are used for common variety uses, like abrasives, soil amendments, lightweight aggregates, and cinder block and with the three deposits in the western U.S. that are producing natural pozzolan. Construction sand and gravel deposits and some pumice deposits produce materials used as extenders in concrete. The Kirkland tuff is in a class above these deposits though, because the tuff can be used as a pozzolan, to enhance the concrete and its properties and not just extend it. One deposit in each of Nevada, New Mexico, and Idaho produce natural pozzolans. Two are pumice deposits and the third a pumiceous tuff. The analytical data show that the Kirkland tuff performs as well or better than this elite class of natural pozzolan deposits.

Market information shows that the natural pozzolan market is dramatically expanding because the supply of class F fly ash is being gradually exhausted. Fly ash is a byproduct from coal fired power plants, and as the plants switch to cleaner fuels, supply of fly ash is dwindling. Fly ash and ground granulated blast furnace slag have dominated the supplementary cementitious material market for decades, but a natural pozzolan resurgence is building along with a change in paradigm in the cement and concrete industries which are used to using fly ash. The change in the industry is only in its infancy, so prices for natural pozzolan have not risen much beyond the price for fly ash.

Even so, this price is well above the price received for common variety deposit material like construction sand and gravel, lightweight aggregate, and cinders used in the construction industry. As the demand for natural pozzolan increases, the price probably will rise. Thus, the physical and chemical characteristics of the Kirkland tuff impart to it a distinct and special value in the marketplace.

### (b) (4)

(b)(4)

Relative to the cost of producing an aggregate extender for concrete, these costs are high. However, subtracting the cost from the sales price gives a value differential. Common variety materials typically have a value differential of only a few dollars per ton or less. (b) (4)

This sets the Kirkland tuff apart even from other types of deposits like diatomaceous earth and siliceous shales which also can be used as

pozzolans but require calcination of crystalline minerals to achieve enough glass to be reactive as a pozzolan.

Thus, the Kirkland tuff on the Capital association placer mining claim has unique, intrinsic physical and chemical characteristics that impart to it a distinct and special value in the market place, reflected in both a high sales price and high differential value between overall cost and price. In my opinion, it meets the guidelines established by the Common Varieties Act and clarified in case law to be an uncommon variety deposit locatable under the General Mining Law.

### Introduction

# Purpose

Kirkland Mining Company (Kirkland) intends to file a mining plan of operations with the U.S. Bureau of Land Management (BLM) to develop its deposit on unpatented mining claims in sections 28 and 33, township 13 north, range 4 west, Gila and Salt River Meridian (Sec. 28 and 33, T. 13 N., R. 4 W., G&SR), Yavapai County, Arizona. The BLM regulations at Title 43, Code of Federal Regulations, Subpart 3809.101 (a) (abbreviated 43 CFR 3809.101 (a)) require that the BLM complete a mineral examination report to determine whether the subject mineral is locatable under the 1872 Mining Law, as amended, before it can process a mining plan of operations. The purpose of this report is to provide BLM information and supplemental data to assist in the completion of the required mineral examination report (common variety determination).

## Legal Framework

The Mining Law of 1872 (17 Stat. 91, 30 U.S.C. §§ 22 *et seq.*) provides that valuable mineral deposits can be embraced by citizens of the United States (U.S.) or U.S. companies through a process of location of mining claims. The original law applied to most mineral commodities. However, during the course of several decades, Congress amended the law to include only specific minerals and mineral substances. On July 23, 1955, Congress enacted the Common Varieties Act (also known as the Surface Resources Act of 1955; 30 U.S.C. §§ 611-615) which removed from location and operations of the mining law so called common varieties of minerals like sand, stone, gravel, pumice, pumicite, and cinders unless the deposit has some property giving it distinct and special value (30 U.S.C. § 611). The language of the law, definition of the term "common varieties" of materials not subject to location, and definition of "uncommon varieties" which could be located under the mining law, have been interpreted in numerous court cases since enactment of the Common Varieties Act.

Through court rulings, the guidelines for distinguishing between common and uncommon varieties of mineral materials have been developed. These were summarized in the McClarty case (McClarty vs. Secretary of the Interior, 408 F. 2d. 907 (9th Cir. 1969)):

1) there must be a comparison of the mineral deposit in question with other deposits of such minerals generally;

2) the mineral deposit in question must have a unique property;

3) the unique property must give the deposit a distinct and special value;

4) if the special value is for uses to which ordinary varieties of the mineral are put, the deposit must have some distinct and special value for such use; and

5) the distinct and special value must be reflected by the higher price which the material commands in the market place.

In the McClarty case, the court also ruled that the distinct and special value also may be reflected by a reduction in the cost or overhead to produce the deposit in question. The unique property must be an intrinsic characteristic of the deposit (e.g., compressive strength of stone) and not extrinsic (e.g., proximity to market).

The BLM mineral examination report required by 43 CFR 3809.101 (a) is a determination whether the subject deposit is a common or uncommon variety deposit.

### Assignment

This assignment was an outgrowth from a meeting in Phoenix, Arizona, with Kirkland and the law firm Fennemore Craig, P.C. (Fennemore Craig), on October 6, 2015. Kirkland had approached the BLM, Hassayampa Field Office, in early 2015 with a proposal to develop the subject deposit. BLM had outlined the permit process and federal regulatory requirements for Kirkland, and Kirkland sought assistance from counsel through Fennemore Craig. One component of the process was the compilation of the required mineral examination report, so Fennemore Craig and Kirkland asked me to attend the meeting and potentially assist the process because I had worked for BLM as a mineral examiner.

The mineral report process and updated BLM guidance were obtained from Jeff Garrett, Arizona State Office BLM, Geologist and Mineral Examiner, on October 15, 2015. I was assigned to write this report by Kirkland on June 20, 2016, to assist Kirkland and the BLM and to expedite the mineral report process. This report conforms to current BLM guidelines, so it can be used as a supplement to the BLM mineral examination report required by 43 CFR 3809.101 (a).

### Scope

The mineral deposit in this case is a deposit of volcanic tuff situated approximately 1.5 miles northeast of the community of Kirkland, Yavapai County, Arizona. The mineral deposit is held under both placer and lode unpatented mining claims that embrace portions of Secs. 28 and 33, T. 13 N., R. 4 W., G&SRM (Appendix B). The Capital association placer mining claim encompasses approximately 160 acres in the SW 1/4 of Sec. 28, and the Homesteak association placer mining claim encompasses approximately 160 acres in the SW 1/4 of Sec. 33. Both placer mining claims currently are owned by eight individuals of the Zouvas family. The Capital placer mining claim is partially overlain with the Capital One through Capital Eight lode mining claims, and the Homesteak placer mining claim is partially overlain is partially overlain with the Homesteak #1 through Homesteak #8 lode mining claims. All the lode mining claims are owned by Kirkland (Appendix B).

The deposit has been and is being developed for its value in industrial markets and not for the value of metals or a specific chemical element. Thus, it is properly categorized as a "stone" and falls within the group of "minerals" subject to the Common Varieties Act. Mineral deposits of this group are properly located as placer mining claims under the Building Stone Placer Act of 1892 as amended (30 USC § 161).

A proposal by Kirkland to develop a mine in the SW 1/4 of Sec. 28, T. 13 N., R. 4 W., G&SRM, within the boundaries of the Capital placer mining claim and Capital One through Capital Eight lode mining claims, prompted this report. The BLM mineral examination report required by 43 CFR 3809.101 (a) would not address the efficacy of the mining claims. The required report is meant to address the question of whether the deposit at that location meets the criteria for an uncommon variety of mineral and is, thus, locatable. This report provides data and information to assist in the answer to that question and provides an opinion about the character of the deposit. Thus, this report is not a mining claim validity determination that addresses whether a discovery of the valuable mineral deposit has been made in the mining claims; it addresses instead whether the subject deposit meets the criteria for an uncommon variety and is potentially locatable under the mining law. This report should not be interpreted nor used for any other purpose.

The data and information contained herein apply only to the portion of the deposit embraced within the Capital association placer mining claim. The deposit within the boundaries of the Homesteak placer mining claim is an extension of the deposit on the Capital placer mining claim; however, the majority of the geologic data, sampling, results of sample testing and analysis, and information about markets has been focused on the deposit in the Capital placer mining claim where Kirkland intends to begin development of the deposit. Based on field observations and limited testing, the deposit on the Homesteak placer mining claim is very similar lithologically and most likely has similar physical and chemical characteristics to the portion of the deposit on the Capital placer mining claim. However, the scope of this report and opinion whether the deposit is potentially locatable is limited at this time to the deposit underlying the Capital association placer mining claim.

### Land Status and Record Data

The land referred in this report includes the SW/4, Sec. 28, and the NW/4, Sec. 33, T. 13 N., R. 4 W., G&SRM, Yavapai County, Arizona. Both the surface and subsurface estates of these lands are administered by the BLM (cf. master title plats in Appendix A). Lands surrounding the subject parcels includes BLM administered land, privately owned surface and subsurface estates, state trust lands administered by the Arizona State Land Department, or split estate lands with private or state surface and federally administered subsurface (cf. historical land status map in Appendix A). Both the parcels in Secs. 28 and 33 are open to location under the 1872 Mining Law as amended ((17 Stat. 91, 30 U.S.C. §§ 22 et seq.).

Current mining claims in good standing embrace the subject lands in Secs. 28 and 33 (Appendix B). The Capital Association Placer Mining Claim (AMC 367119) (Capital MC) encompasses the SW/4, Sec. 28, and the Homesteak Association Placer Mining Claim (AMC 371346) (Homesteak MC) encompasses the NW/4, Sec. 33, T. 13 N., R. 4 W., G&SRM. Both placer mining claims are owned by the Zouvas family. The current Capital MC was located July 15, 2005, and the current Homesteak MC was located April 2, 2006. However, the area embraced by the Homesteak and Capital association placer mining claims has been under continuous mining claim ownership by the Zouvas family since 1991.

Both placer mining claims have been overstaked with lode mining claims. Kirkland located the Capital One through Capital Eight lode mining claims (AMC 428988 through 428995) in the SW/4 of Sec. 28 on May 11, 2014, and the Homesteak #1 through Homesteak #8 (AMC 432946 through 432953) in the NW/4, Sec. 33, on March 11, 2015 (Appendix B). Maintenance fees and all required county documents are current for both the placer and lode mining claims.

This common variety determination applies only to the Capital MC (AMC 367119).

# **Physical Features and Access**

The Kirkland tuff deposit is located approximately 1.5 miles northeast of Kirkland, Arizona (Fig. 1). The terrain is moderately rugged and characterized by a dendritic drainage pattern with low profile washes incised into bedrock (Figs. 2 and 3). Rounded, low profile hills and ridges separate the washes, although locally, where the bedrock is more indurated and differential erosion has occurred, straight walled buttes rise above the washes, some with 100 foot cliffs (Fig.

4, 5, and 6). Volcanic tuff makes up most of the outcrops on the mining claim and typically weathers to the low, rounded hills (Fig. 7 through 15). Historic mining operations left a quarry and stockpile of material from the quarry in the west central part of the Capital mining claim and two smaller quarries in the southern part of the mining claim (Fig. 3). Otherwise, the terrain is undisturbed.

Elevations vary from approximately 3910 feet above mean sea level (amsl) at the southwestern corner of the claim to about 4200 amsl at the northeastern corner of the claim. Climate is typically mild with hot, dry summers and rains during the monsoon in August and September and cold, dry winters with periodic snowfall less than five inches. Summertime temperatures can reach 105° F. during the day, and winter night temperatures can dip to 0°; however, winter night time temperatures are typically in the 20 to 30° F. range.

Access to the site is afforded by Arizona highway 89 from either Prescott or Wickenburg, Arizona, (Fig. 1), then by light duty, paved two lane road known as the South Kirkland Valley Road (Arizona Highway 96) from highway 89 to Kirkland, Arizona (Fig. 2). South Iron Springs Road northeast from Kirkland is the access to the mining claims. A two track access road exits east off the Iron Springs Road approximately 1.7 miles northeast of Kirkland (Fig. 2). The land surrounding the access road and the access to the mining claims is owned by Kirkland Mining Company. This road enters the west central part of the Capital MC. Access is not impeded except that Kirkland Mining Company maintains a locked gate at the western boundary of the Capital MC.

A Burlington Northern-Santa Fe railway spur runs along Iron Springs Road to Kirkland.

### Field Work, Sampling Procedures, and Analytical Work

### **Field Work**

Work on this report began on June 21, 2016, immediately after assignment from Kirkland. I obtained company files from Kirkland, which included geologic survey, geologic reports, and analytical data, and scheduled a field examination.

I conducted a full day field examination on June 26, 2016, with Corina Wilson, Field Assistant, Burch Consulting Services, LLC, Areta Zouvas, Principal, Kirkland Mining Company, and Brian Hampton, Quarry Manager, Kirkland Mining Company. We toured the entire Capital MC and a portion of the Homesteak MC and verified geologic mapping from Cortright and Abramson-Beck (2015), verified sample and drill hole sites, and verified drill hole logs from Sandwell-Weiss (2016) through examination of selected core sections from each of 10 drill holes. Rocks and structures were described in the field. The tuff was classified in accordance with Fisher and Frost (2007, p. 139), and the basaltic rocks were classified in accordance with Travis (1955). Rock colors were described in accordance with Goddard (1984).

After the field examination, we began compilation of mining company records and compiled a list of potential commodities that could be considered from the Kirkland tuff deposit. After review of literature for abrasives, aggregates, absorbents, soil and agriculture amendments, cement, and pozzolans, we conducted an exhaustive literature search for industrial mineral deposits in the western U.S. We focused on deposits with similar lithology and deposits with

commodities similar to those that could be produced from Kirkland with a focus on deposits of tuff, pumice, pumicite, diatomaceous earth, opaline cherts, perlite, siliceous shale, and aggregates.

For deposit, market, pricing, and mining and processing cost data, I obtained records from operating companies and conducted phone interviews with producers and marketing consultants in the cement and natural pozzolan industries, mine operators and mine owners of several deposits, and agents with companies producing and selling other commodities to the construction industries, e.g., aggregates and limestone. Data was also obtained from internet websites for companies and from geological and mineral resource agencies for the western states. I also interviewed BLM and U.S. Forest Service (USFS) staff working on common variety determination reports or USFS classification reports for similar commodities. Personal communication references are given in text. Internet and literature data sources are cited in text and appear in the references cited section of this report.

### Sampling



A few samples were collected in the 1980s and 1990s by previous owners of the site, and some of these were chemically analyzed; however, sample protocols and locations are uncertain so they are referred only generally in this report.





# **Analytical Work**









### **Regional Geology and Mining History**

### **Regional Geology**

The subject Kirkland tuff deposit lies in the central section basin part of the Arizona Transition Zone, a geomorphic province sandwiched between the Colorado Plateau province to the northeast and the Basin and Range province to the southwest (Fig. 16). The transition zone trends northwest through the central part of the state. It contains rock units and geologic structures transitional to those on the Colorado Plateau and the Basin and Range. Transition Zone Phanerozoic rocks are similar to those of the Colorado Plateau with the exception that the younger sedimentary rocks typical of the Colorado Plateau have been removed by erosion from most of the transition zone. The erosion locally exposed the older Precambrian granitic and metamorphic basement rocks.

Major tectonic events and uplift occurred in this region beginning in the early Cenozoic Era about 65 million years ago (mya), and crustal extension, which began about 20 mya, continues in the Basin and Range. Intermontane basins formed in the region beginning in the Oligocene Epoch (34-23 mya) and were the site for deposition of sedimentary rocks shed from surrounding highlands. Volcanism occurred intermittently beginning in the Miocene Epoch (23-5 mya) due to the crustal extension, and ash and volcaniclastic rocks were deposited along with the sedimentary rocks in the intermontane basins (Nations and Stump, 1996, p. 170).

Rocks in the vicinity of the Kirkland area consist of older, metamorphosed Precambrian basalt, tonalite, and granite overlain with Miocene sedimentary and volcanic rocks (Fig. 17). Locally, the younger sedimentary and volcanic rocks that formed in the Tertiary basins are juxtaposed along normal faults against the older Precambrian rocks. Both older and younger rocks comprise the bedrock in the region. Pliocene (5.3-2.5 mya), Pleistocene (2.5 my-12,000 years ago), and Holocene (Recent) sedimentary rocks and alluvium overlie the bedrock in the Kirkland area (Fig. 17).

17

### **Regional Mining History**

Mining has occurred in this region of Arizona since the late 1800s. Metal mines were developed in the Bradshaw Mountains a few miles east and near Yarnell, Congress, Stanton, and Wickenburg a few miles to the south of Kirkland. As the towns and cities in this part of Arizona grew in the early 1900s, the need for industrial minerals arose to support a growing infrastructure. A dimension stone industry developed north of Prescott near Chino in the early 1900s, and gravel and aggregate sources were developed in the 1940s and 1950s as roads were improved in this part of the state and construction materials were needed in Flagstaff, Prescott, and Phoenix. The current cement and concrete industry expanded dramatically from the 1960s to the present. Industrial mineral production from the region now includes (but is not limited to) aggregates and light weight aggregates, landscape stone and boulders, dimension stone, clay, cinders, pumice, gypsum, limestone, and industrial sand (Fig. 18).

Mining claims have existed at the Kirkland tuff deposit site since 1896, and dimension stone to make facing and light weight block most likely was quarried from the site in those early days. Stone from the Kirkland site was used in the construction of the Arizona State Capitol building, probably at first construction in 1901 and definitely in the addition in the 1950s (Arizona Geological Survey, 2015, 1958 Engineers Report, Rynearson Kirkland Quarry file; Townsend, 1961, p. 29). Buildings in Congress and Yarnell also were constructed with the sawed stone from Kirkland in the early 1900s.

Cement currently is manufactured by Drake Cement at a plant approximately 25 miles north of Prescott with industrial mineral commodities mostly produced in the western part of Arizona and adjoining states. Also, Kirkland is situated in close proximity to growing towns and cities with demand for industrial mineral commodities.

### **Geology and Mineral Deposits**

### Geology

The Kirkland tuff deposit has been prospected since the late 1800s; however, no detailed geologic studies were conducted at the subject site until it was acquired by the Zouvas family. Randall (1974) mapped rocks adjacent and to the west of the deposit as part of a University of Arizona Master's thesis and provided a description of the tuff based on a measured stratigraphic section on what is now the Homesteak MC (Randall, 1974, p. 12-13); however, his maps did not encompass the land now covered by the Capital or Homesteak MCs.

conducted a geologic reconnaissance of the site for Kirkland and followed up that study with a drilling program and summary report (b) (4)

conducted the most thorough recent work and mapped the lode mining claims on both the Capital and Homesteak MCs. Their maps encompass most of the area within the two placer claims.

No detailed geologic mapping was done for this report; however, I conducted a field examination and verified the mapping that was completed by (b) (4) The geologic map that covers most of the Capital MC is shown in Fig. 19.



![](_page_19_Picture_0.jpeg)

![](_page_20_Picture_0.jpeg)

#### **Mineral Deposits**

No metallic mineral deposits occur within the Capital MC. The rocks themselves, the stone, make up the potential mineral deposits.

Basalt, because of its weight, is sometimes used as rip rap or is crushed and used as railroad ballast. Although state highways and a spur railroad line exist near the Capital MC, no new construction is anticipated. Most likely, no demand exists for the use of the basalt from the mining claim, and the uses for basalt typically are considered common variety uses. Thus, the basalt will not be considered further in this report as a viable mineral deposit.

Deposits of gravel can be used as aggregate, but only a small volume of gravel exists on the Capital MC along the washes. Additionally, usage of gravel typically is a common variety use. Thus, gravel deposits on the Capital MC will not be considered further in this report as a viable mineral deposit.

The tuff on the Capital MC must be considered a potentially viable mineral deposit. This tuff historically was used as a dimension stone (Townsend, 1961, p. 29) and was prospected and mined as an absorbent from about 1979 to 1984 (Arizona Geological Survey, 2015, Kirkland Quarry file). (b) (4)

(b) (4)

Thus, the lithic tuff described above constitutes the mineral deposit(s) on the Capital MC and will be considered in this supplement to the common variety determination.

![](_page_21_Picture_1.jpeg)

![](_page_22_Picture_0.jpeg)

![](_page_23_Picture_0.jpeg)

#### Natural Pozzolan

Pozzolans are used in the cement and concrete industries. They are siliceous or siliceous and aluminous materials that alone possess little or no cementitious value, but will, in a finely divided form and in the presence of water, chemically react with calcium hydroxide, such as found in cement at ordinary temperatures, to form compounds possessing hydraulic cementitious properties (Hoffman, 2006, p. 1161). The intrinsic characteristics of the tuff on the Capital MC allow it to be used as a natural pozzolan, so below is an explanation that outlines pertinent information about the chemistry of cement, its manufacture, pozzolans and how pozzolans are used, and how the intrinsic characteristics of the Kirkland tuff will allow it to be considered a natural pozzolan.

#### **Cement - General**

Cement is a powder, used as a binder, a substance that sets and hardens and binds other materials together because of its chemical characteristics. It often is used in the production of mortar used in masonry and in the production of concrete, which is a mixture of the cement and an aggregate used for strong building materials in construction. Although the terms "cement" and "concrete"

often are used interchangeably, cement is actually an ingredient of concrete. Cements are the binding agents in concretes and mortars. Concrete is an artificial rock-like material, basically a mixture of coarse aggregate (gravel or crushed stone), fine aggregate (sand), cement, air, and water. Cements used in construction are usually inorganic and are often lime based.

Two general types of cement exist, non-hydraulic and hydraulic, depending on the ability of the cement to set in the presence of water. Non-hydraulic cement will not set in wet conditions or underwater. Most types of non-hydraulic cement set as they dry and react with  $CO_2$  in the air. Non-hydraulic cement is resistant to attack by chemicals after setting. In contrast, hydraulic cements set and become adhesive due to a chemical reaction between the dry ingredients and water. The chemical reaction results in mineral hydrates that are not very water-soluble, durable in water, and relatively safe from chemical attack (Wikipedia,

https://en.wikipedia.org/wiki/Cement, retrieved December 27, 2016). Hydraulic cements are the binding agents in most concretes and most mortars and are thus common and critically important construction materials. Pozzolans sometimes are used with hydraulic cements but not with non-hydraulic cements, so non-hydraulic cements will not be discussed further.

Portland cement (also known as ordinary portland cement (OPC)), once used as a specific product name, is now used as a general term to describe a variety of hydraulic cements which will set and harden by reacting chemically with water through hydration (Mitsubishi Cement Corporation (MCC), 2006, p. 2). Portland cement is the most commonly manufactured and used hydraulic cement in the United States and the world.

### **Portland Cement Manufacture**

Portland cement manufacturing is a two-step process beginning with the manufacture of "clinker" followed by the fine grinding of the clinker with gypsum and other additives to make the finished cement product. It is manufactured through the blending of mineral raw materials at high temperatures in cement rotary kilns. Rotary kilns produce the intermediate product clinker. By modifying the raw material mix and, to some degree, the temperature of manufacture, slight compositional variations in the clinker can be achieved to produce portland cements with varying properties (MCC, 2006, p. 2). Fig. 22 provides a generalized flow diagram of the cement manufacturing process.

The first step in clinker manufacture is the quarrying, crushing, and proportioning of raw materials. Calcium oxide (CaO or simply C in shorthand) is the primary ingredient in clinker, comprising about 65% of clinker by mass. A cement plant typically examines its source of C and determines what other oxides need to be added to achieve the desired clinker composition. The raw materials for clinker manufacture consist primarily of materials that supply four primary oxides: calcium oxide (CaO), silicon dioxide (SiO<sub>2</sub>), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), and ferric oxide (Fe<sub>2</sub>O<sub>3</sub>). Raw materials typically consist of calcium carbonate (CaCO<sub>3</sub>; mainly occurring as limestone, marine shells, or chalk deposits), bauxite, shale, or clay (providing aluminum oxide and silica), sand (providing silica), and iron ore or mill scale (Fe<sub>2</sub>O<sub>3</sub>). The composition of the raw mix typically includes about 80% calcium carbonate, about 10% to 15% silica, and small amounts of alumina and iron. Depending on the quality, quantity, and availability of these oxides to the facility, other raw materials, referred to as accessory or sweetener materials, are added to correct for any deficiencies in the primary raw materials.

Certain types of fuel burned in the cement kiln can also contribute oxides (e.g., ash from coal combustion can contribute silica oxides or steel belts in waste tires used for fuel can contribute iron oxide).

Due to the low unit value of raw materials, they typically are mined within a few miles of the cement plant because the cost of transport renders long-distance transport of low-cost raw materials uneconomical. Historically, even materials like pumice, which may be considered a potential natural pozzolan today, were added as accessory materials to the raw mix. Raw mix and accessory materials typically are low priced materials, however, so the use of materials that may be considered pozzolans has now been discontinued. Simply, pozzolanic materials can be sold at higher value for blending later in the cement manufacturing process, so none are sold today at low value as an accessory material for the raw mix **(b) (4)** 

Once the raw mix, or raw meal, is ground and prepared, it is fed into a cement kiln and converted into the clinker minerals through a thermochemical conversion, referred as pyroprocessing, because it involves direct flame interaction. The mixture is heated in kilns that are long rotating steel cylinders on an incline. The mixture of raw materials enters at the high end of the cylinder and slowly moves along the length of the kiln (up to 180 meters in length) due to the constant rotation and inclination. Temperatures range from 1,600 to 1,800° C., and the mix can be in the kiln for two hours. The result of the sintering process is a gray-black fused pebble or nodule. Table 2 illustrates a typical composition of clinker.

Table 2. Chemical shorthand and composition of clinker and portland cement. Table 2 shows stoichiometric shorthand terms for the major constituent oxides used in the cement industry. For clinker, the oxide compositions generally would not vary from the rough averages shown by more than 2% to 4%. The oxide composition of portland cement would vary slightly depending on its actual gypsum fraction or whether any other additives are present. Table modified after van Oss (2005, p. 14).

| Oxide<br>Formula               | Shorthand<br>Notation  | Percentage by Mass in<br>Clinker | Percentage by<br>Mass in<br>Cement* |
|--------------------------------|------------------------|----------------------------------|-------------------------------------|
| CaO                            | С                      | 65                               | 63.4                                |
| SiO <sub>2</sub>               | S                      | 22                               | 20.9                                |
| Al <sub>2</sub> O <sub>3</sub> | А                      | 6                                | 5.7                                 |
| Fe <sub>2</sub> O <sub>3</sub> | F                      | 3                                | 3.0                                 |
| MgO                            | М                      | 2                                | 1.9                                 |
| $K_2O + Na_2O$                 | K + N                  | 0.6                              | 0.6                                 |
| Other                          | (S)                    | 1.4                              | 3.6                                 |
| H <sub>2</sub> O               | Н                      | "nil"                            | 1.0                                 |
| * Based of                     | n clinker shown plus 5 | % addition of gypsum (CaSO4      | ·2H2O)                              |

On average, it takes about 1.7 tons of nonfuel raw materials to produce 1.0 ton of clinker. Of the 1.7 tons of raw materials, approximately 1.5 tons is limestone or calcium oxide rich rock. The lost mass takes the form of carbon dioxide ( $CO_2$ ) driven off by the calcination of limestone

and the generation of cement kiln dust (CKD). Nearly one ton of  $CO_2$  is produced for every ton of clinker manufactured. The CKD that is produced during clinker manufacture is carried "up the stack" and captured by emission control devices. A large portion of the CKD, though not all of it, is returned to the kiln as part of the feed stream (MCC, 2006, p. 10).

After cooling to about 100° C, the clinker is mixed with gypsum or anhydrite (typically 3% to 7%) and milled in a grinding mill typically referred to as a finish mill. Gypsum is added to lubricate the clinker in the grinding process (gypsum is a soft mineral), and to later moderate the hydration process when the cement is hardening during use. Other materials may be added during the grinding process to make the blended cements described below, or the ground clinker-gypsum mix may be sold directly to users for production of concrete (Fig. 22). Generally, separate grinding and/or blending finish mill lines will be maintained at a plant for each of its major product classes (e.g., finished portland cements, blended cements, masonry cements, ground slag). Additives that commonly require grinding at the mill include gypsum, limestone, granulated blast furnace slag, and natural pozzolans. Additives that generally do not require significant grinding include coal fly ash, ground granulated blast furnace slag (GGBFS), and silica fume, but the finish mill does provide intimate mixing of these with the portland cement base (MCC, 2006, p. 10). Additives are described below in the section on blended cements.

### **Cement Chemistry**

The major oxides from the raw mix combine chemically in the kiln at high temperatures essentially into just four cement or clinker minerals, and the key chemical reaction that defines portland cement from other hydraulic limes takes place in the kiln at high temperatures. During sintering, the belite (Ca<sub>2</sub>SiO<sub>4</sub>) combines with CaO to form alite (Ca<sub>3</sub>SiO<sub>5</sub>)(Wikipedia, https://en.wikipedia.org/wiki/Cement, retrieved December 27, 2016).

Table 3 provides the chemical formulas and nomenclature for the major cement oxides and minerals and the function of each in cement mixtures. The minerals in clinker serve different functions in the manufacturing process or impart varying final properties to the cement. The proportion of C3S, for example, determines the degree of early strength development of the cement. The ferrite mineral's (C4AF) primary purpose, on the other hand, is to lower the temperature required in the kiln to form the C3S mineral, and really does not impart a specific property to the cement. Generally, Al, Fe, and Mg oxides are present as a flux allowing the calcium silicates to form at a lower temperature; they contribute very little to the strength of the cement. For special cements, like sulfate resistant cements, the manufacturer would limit the amount of C3A that is formed. For low heat types, the manufacturer would limit the C3S that is-formed (Wikipedia, https://en.wikipedia.org/wiki/Portland\_cement, retrieved December 22, 2016). Thus, it is the ratios of the four minerals (and gypsum and other additives) that determine the varying properties of different types of portland cements.

Table 3. Typical mineralogical composition of modern portland cement. The formulas represent averages, ignoring impurities commonly found in actual clinker. Table modified after van Oss (2005, p. 15).

| Chemical<br>Formula                            | Oxide<br>Formula   | Shorthand<br>Notation | Description  | Typical<br>Percentage | Mineral Function   |
|--|--|-----------------------|--|-----------------------|--|
| Ca <sub>3</sub> SiO <sub>5</sub>               | (CaO) <sub>3</sub> ·SiO <sub>2</sub>   | C3S                   | Tricalcium<br>silicate (alite)                                   | 50-<br>70             | Hydrates quickly<br>and imparts early<br>strength and set  |
| Ca <sub>2</sub> SiO <sub>4</sub>               | (CaO) <sub>2</sub> ·SiO <sub>2</sub>   | C2S                   | Dicalcium<br>silicate (belite)                                   | 10-<br>30             | Hydrates slowly<br>and imparts long<br>term (ages<br>beyond 1 week)<br>strength.   |
| Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub> | (CaO) <sub>3</sub> ·Al <sub>2</sub> O <sub>3</sub>                                     | C3A                   | Tricalcium<br>aluminate<br>(celite)                              | 3-<br>13              | Hydrates almost<br>instantaneously<br>and very<br>exothermically<br>unless temporarily<br>suppressed by<br>adding gypsum.<br>Contributes to early<br>strength and set. |
| Ca4Al2Fe2O10                                   | (CaO) <sub>4</sub> ·Al <sub>2</sub> O <sub>3</sub> ·<br>Fe <sub>2</sub> O <sub>3</sub> | C4AF                  | Tetracalcium<br>aluminoferrite<br>(ferrite or<br>Brownmillerite) | 5-<br>15              | Hydrates quickly.<br>Acts as a flux in<br>clinker<br>manufacture.<br>Imparts gray<br>color.  |
| CaSO <sub>4</sub> .<br>2H <sub>2</sub> O       | CaO· SO <sub>3</sub> ·<br>2 H <sub>2</sub> O   | C S H2                | Calcium sulfate<br>dihydrate<br>(gypsum)                         | 3-7                   | Interground with<br>clinker to make<br>portland cement.<br>Can substitute<br>anhydrite (C S ).<br>Controls early set.  |
| CaSO <sub>4</sub>                              | CaO· SO <sub>3</sub>   | CS                    | Anhydrous<br>calcium sulfate<br>(anhydrite)                      | 0.2-<br>2             | Substitute for<br>gypsum   |

Proportions of the cement minerals and additives determine the reactions that occur when cement is used in construction. Cement sets or hardens when the cement mixture derived from clinker and additives is mixed with water. Contrary to popular perceptions, hydraulic cements do not set by drying out. Cement sets through a series of hydration reactions caused by combining water and the minerals shown in Table 3. The constituents slowly hydrate, and the cement solidifies through a curing process. During the curing process, the interlocking of the hydrate compounds give hardened cement its strength. Maintaining the appropriate moisture content during the curing process is critically important to strength. If hydraulic cements dry out during curing, the resulting product can be significantly weakened.

The chemical reactions that occur during cement cure can be complex, but basic understanding is necessary to illustrate the role that additives like pozzolans play in cement manufacture for specific applications. When water is added to the cement mix, typically the following reactions occur (modified from (Pennsylvania State University,

http://www.engr.psu.edu/ce/courses/ce584/concrete/library/construction/curing/Hydration.htm, retrieved February 2, 2017):

• The tricalcium aluminate reacts with the gypsum in the presence of water to produce the mineral ettringite and heat:

Tricalcium aluminate + gypsum + water  $\circledast$  ettringite + heat  $C_{3}A + 3C\underline{S}H_{2} + 26H \circledast C_{6}AS_{3}H_{32}, DH = 207 \text{ cal/g} (i)$ 

Ettringite consists of long crystals that are only stable in a solution with gypsum. The compound does not contribute to the strength of the cement glue.

• The tricalcium silicate (alite) is hydrated to produce calcium silicate hydrates, lime and heat:

*Tricalcium silicate* + water ® calcium silicate hydrate + lime + heat  $2C_3S + 6H \otimes C_3\underline{S}_2H_3 + 3CH$ , DH = 120 cal/g (ii)

The CSH has a short-networked fiber structure which contributes greatly to the initial strength of the cement glue.

• Once all the gypsum is used up as per reaction (i), the ettringite becomes unstable and reacts with any remaining tricalcium aluminate to form monosulfate aluminate hydrate crystals:

*Tricalcium aluminate* + *ettringite* + *water*  $\circledast$  *monosulfate aluminate hydrate*  $2C_{3}A + 3 C_{6}AS_{3}H_{32} + 22H \circledast 3C_{4}ASH_{18}$ ,

The monosulfate crystals are only stable in a sulfate deficient solution. In the presence of sulfates, the crystals resort back into ettringite, whose crystals are two-and-a-half times the size of the monosulfate. It is this increase in size that causes cracking when cement is subjected to sulfate attack.

• The belite (dicalcium silicate) also hydrates to form calcium silicate hydrates and heat:

Dicalcium silicates + water  $\mathbb{B}$  calcium silicate hydrate + lime  $C_2S + 4H \mathbb{B} C_3S_2H_3 + CH, DH = 62 \text{ cal/g}$ 

Like in reaction (ii), the calcium silicate hydrates contribute to the strength of the cement paste. This reaction generates less heat and proceeds at a slower rate, meaning that the

contribution of  $C_2S$  to the strength of the cement paste will be slow initially. This compound is however responsible for the long-term strength of portland cement concrete.

- The ferrite undergoes two progressive reactions with the gypsum:
  - in the first of the reactions, the ettringite reacts with the gypsum and water to form ettringite, lime and alumina hydroxides, i.e.
    - *Ferrite* + gypsum + water ® ettringite + ferric aluminum hydroxide + lime
    - $C_4AF + 3C\underline{S}H_2 + 3H \otimes C_6(A,F)\underline{S}_3H_{32} + (A,F)H_3 + CH$
    - the ferrite further reacts with the ettringite formed above to produce garnets, i.e.
      - *Ferrite* + *ettringite* + *lime* + *water* ® *garnets*
      - $C_4AF + C_6(A,F)S_3H_{32} + 2CH + 23H \otimes 3C_4(A,F)SH_{18} + (A,F)H_3$

The garnets only take up space and do not in any way contribute to the strength of the cement paste.

Each of the compounds used in cement play a role in the rate and extent of the hydration reactions, the heat produced during curing, and both the early and late strength of the cement. For example, the amount of gypsum added can be used to accelerate (less gypsum) or retard (more gypsum) the setting process of portland cement. Additionally, magnesia in portland cement is somewhat critical. It is innocuous at low concentrations; however, as the magnesia concentration in the cement becomes higher, magnesium compounds formed after slaking (hydration) and mixing with aggregates to form concrete tend to expand and displace cementing minerals. These reactions can adversely affect the strength of the concrete (MCC, 2006, p. 15). Also, the color of the cement can be controlled by adding other materials or limiting certain elements. Thus, cements can be tailored to meet engineering specifications and performance standards by varying the materials used to make a particular type of cement.

### **Types of Portland Cement**

Similar varieties of portland cement are made in many parts of the world but go by different names. In the U.S., the different varieties of portland cement are denoted per the ASTM C150 standard and specifications and AASHTO M85 (MCC, 2006, p. 15). Table 4 illustrates the general types of cement, their range of compositions, and general properties.

The types of cements are denoted based on their chemistry; however, they are further defined based on physical character, additives, and performance in application. For example, the physical characteristics of the particles in the cement mix for the various types can also affect the cement properties during slaking. Portland cement typically consists of individual angular particles with a range of sizes, the result of grinding in the finish mill. Approximately 95% of cement particles are smaller than 45 microns ( $\mu$ m), with the average particle around 15  $\mu$ m. The fineness of cement affects the amount of heat released during hydration. Greater cement fineness (smaller particle size) increases the rate at which cement hydrates and thus accelerates strength development. Except for AASHTO M85, most cement standards do not have a

Table 4. Typical range in mineral composition and properties in types of portland cements. Table adopted from van Oss (2005, p. 15)<del>.</del>

| ASTM C-150   | C     | linker Mine | ral Percent* | Properties of Comput |   |
|--|-------|-------------|--------------|----------------------|---|
| Cement Type  | C3S   | C2S         | C3A          | C4AF                 | Froperties of Cement                                    |
| I  | 50-65 | 10-30       | 6-14         | 7-10                 | General purpose   |
| II   | 45-65 | 7-30        | 2-8          | 10-12                | Moderate heat of hydration, moderate sulfate resistance |
| III  | 55-65 | 5-25        | 5-12         | 5-12                 | High early strength**                                   |
| IV   | 35-45 | 28-35       | 3-4          | 11-18                | Low heat of hydration                                   |
| V  | 40-65 | 15-30       | 1-5          | 10-17                | High sulfate resistance                                 |
| * Range of minerals is empirical and approximate rather than definitional.<br>** High early strength is typically achieved by finer grinding of Type I cement and increasing C3S. Source:<br>van Oss (2005, p. 15) and (b) (4) |       |             |              |                      |   |

maximum limit on fineness, only a minimum. The fineness of Types I through V portland cement are shown in Table 5. Values are expressed according to the Blaine air-permeability test (ASTM C204 or AASHTO T153), which indirectly measures the surface area of particles per unit mass.

Table 5. Typical range of fineness for the general types of portland cement. Table adopted from MCC (2006, p. 8).

| ASTM C - 150<br>Cement Type | Fineness (cr | n2/g, Blaine) |
|-----------------------------|--------------|---------------|
|                             | Range        | Mean          |
| I                           | 3,000-4,210  | 3,690         |
| II                          | 3,180-4,800  | 3,770         |
| III                         | 3,900-6,440  | 5,480         |
| IV                          | 3,190-3,620  | 3,400         |
| V                           | 2,750-4,300  | 3,730         |

The different cement types are used to meet the requirements of specific applications.

Type I portland cement is a general-purpose cement suitable for all uses. In some countries, type I is known as ordinary portland cement (OPC). It typically is used in general construction projects such as buildings, bridges, floors, pavements, and other precast concrete products. It typically consists of:

| 63.2 % | Calcium Oxide (CaO; burnt calcium carbonate or lime)                    |
|--------|---|
| 21.3 % | Silica (SiO <sub>2</sub> )  |
| 6.0 %  | Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )                        |
| 2.7 %  | Iron Oxide ( $Fe_2O_3$ )  |
| 2.9 %  | Magnesium Oxide (MgO)   |
| 1.8 %  | Sulfur Dioxide (SO <sub>2</sub> ; added as gypsum in the clinker grind) |

Type II portland cement generates less heat at a slower rate and has a moderate resistance to sulfate attack. It is a high-early-strength cement and causes concrete to set and gain strength rapidly. Most (approximately 90%) of the cement produced in the U.S. is type I and type II (MCC, 2006, p. 18).

Type III is chemically and physically similar to type I but it contains more sulfur than type I cements. Type III cements are made to a finer grind to attain high early strengths when used in portland cement concrete. Type III typically consists of:

| 64.3 % | Calcium Oxide (CaO; burnt calcium carbonate or lime)                    |
|--------|---|
| 20.4 % | Silica (SiO <sub>2</sub> )  |
| 5.9 %  | Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )                        |
| 3.1 %  | Iron Oxide ( $Fe_2O_3$ )  |
| 2.0 %  | Magnesium Oxide (MgO)   |
| 2.3 %  | Sulfur Dioxide (SO <sub>2</sub> ; added as gypsum in the clinker grind) |

Type IV portland cement has a low heat of hydration and develops strength at a slower rate than other cement types. This makes type IV ideal for use in dams and other massive concrete structures where there is little chance for heat to escape.

Type V portland cement is used only in concrete structures that will be exposed to severe sulfate action, especially where concrete is exposed to soil and groundwater with a high sulfate content.

Many different cements can be manufactured to meet market specifications and achieve desired results. Suffixes are added to the ASTM C150 type numbers to denote the different types frequently used in industry. For example, for types I, II, and III, the addition of the suffix A (e.g., Type IA) indicates the inclusion of an air entraining agent (MCC, 2006, p. 3). Air entraining agents impart a myriad of tiny bubbles into the concrete containing the hydrated cement. Air in the concrete displaces water in the pore space and reduces freeze-thaw cracking in the concrete resulting in greater concrete strength and longevity (b) (4)

. Also, in practice, many companies market hybrid portland cements like type I/II, a common hybrid that meets the specifications of both types I and II.

Some cements are classified as expansive. Expansive cements are hydraulic cements that expand slightly during the early hardening period after setting. They meet the requirements of ASTM C845 in which it is designated as Type E-1. Although three varieties of expansive cement are designated in the standard as K, M, and S, only K is available in the U.S. Type E-1 (K) contains portland cement, anhydrous tetracalcium trialuminosulfate, calcium sulfate, and uncombined calcium oxide (lime). Expansive cement is used to make shrinkage-compensating concrete that compensates for volume decrease due to drying shrinkage, to induce tensile stress in reinforcement, and to stabilize long-term dimensions of post-tensioned concrete structures. One of the major advantages of using expansive cement is in the control and reduction of drying-shrinkage cracks. Shrinkage-compensating concrete has been of particular interest in bridge deck construction where crack development must be minimized (MCC, 2006, p. 18).

White portland cement is identical to gray portland cement except in color. During the manufacturing process, manufacturers select raw materials that contain only negligible amounts of iron and magnesium oxides, the substances that give gray cement its color. White cement is used whenever architectural considerations specify white or colored concrete or mortar. It typically consists of:

| 65.3 % | Calcium Oxide (CaO; burnt calcium carbonate or lime)                    |
|--------|---|
| 25.5 % | Silica (SiO <sub>2</sub> )  |
| 5.9 %  | Aluminum Oxide (Al <sub>2</sub> O <sub>3</sub> )                        |
| 0.6 %  | Iron Oxide (Fe2O3)  |
| 1.1 %  | Magnesium Oxide (MgO)   |
| 0.1 %  | Sulfur Dioxide (SO <sub>2</sub> ; added as gypsum in the clinker grind) |

A white blended cement may be produced too with the addition of white metakaolin (Wikipedia, https://en.wikipedia.org/wiki/Cement, retrieved January 27, 2017).

Masonry cements are used for preparing bricklaying mortar and stuccos. These types of cements must not be used in concrete. They typically are formulations containing portland clinker and a number of other ingredients that may include limestone, hydrated lime, air entrainers, retarders, waterproofers, and coloring agents and are formulated to yield workable mortars that allow rapid and consistent masonry work. They are designed to produce a controlled bond with masonry blocks (Wikipedia, https://en.wikipedia.org/wiki/Cement, retrieved January 27, 2017).

When portland cement clinker is ground and mixed with other additives to produce a final cement powder for later use in concrete, it is properly termed a cement admixture or blended cement. Types of blended cement are critically important in this report and discussed below.

### **Blended Cements**

The cementitious properties of the portland cement described above can be enhanced by adding other materials which also have cementitious properties. The portland cement can also be extended by other materials to reduce the volume of portland cement used in a particular application (thus reducing the overall cost of construction and the volume of  $CO_2$  produced during sintering) without sacrificing the integrity of the final concrete product. The mixtures of portland cement and other materials comprise the universe of blended cements.

Materials used in the cement industry with cementitious properties used to enhance or extend cement are collectively termed supplementary cementitious materials (SCMs; National Ready Mixed Concrete Association, https://www.nrmca.org/aboutconcrete/cips/30p.pdf, retrieved February 3, 2017). Hydraulic latent cements are those that possess cementitious properties without mixing with other substances but may be enhanced when mixed with other substances. For example, blast furnace slag, the byproduct of a blast furnace in the production of pig iron from iron ore, has some cementitious properties on its own when hydrated. Its properties are dramatically enhanced, however, in the presence of alkali compounds, particularly lime. When the slag is ground, mixed with portland cement, and activated with water, the cementitious properties are enhanced. Thus, SCMs typically are described as finely divided and noncrystalline

or poorly crystalline materials that possess latent cementing properties that are activated in the presence of portland cement and water (Hoffman, 2006, p. 1161).

Pozzolans are similar to supplementary cementitious materials. However, a true pozzolan is a siliceous or siliceous and aluminous material that alone possess little or no cementitious value, but will, in a finely divided form and in the presence of water, chemically react with calcium hydroxide, such as found in cement at ordinary temperatures, to form compounds possessing hydraulic cementitious properties (Hoffman, 2006, p. 1161). A true pozzolan develops cementitious properties in the presence of lime (Ca(OH)<sub>2</sub>), but has none on its own (MCC, 2006, p. 3). Loosely defined, pozzolanic additives or extenders typically are collectively termed supplementary cementitious materials (MCC, 2006, p. 4).

Blended cements (called composite cements in some countries) are intimate mixes of a portland cement base (generally type I) with one or more SCM extenders. The SCM commonly makes up about 5% to 30% by weight of the total blend, but can be higher. Blended cements either can be prepared at a cement plant for sale as a finished blended cement product or by blending with a concrete mix.

In blended cements, the SCMs are activated by the high pH resulting from the hydroxide ions released during the hydration of portland cement. The most commonly used SCMs are certain types of fly ash (from coal-fired power plants), ground granulated blast furnace slag (GGBFS), now increasingly being referred to as slag cement, burned clays, silica fume, and cement kiln dust (CKD)(all described below). In general, incorporation of SCM with portland cement improves the resistance of the concrete to chemical attack, reduces the concrete's porosity, reduces the heat of hydration of the cement (not always an advantage), potentially improves the flowability of concrete, and produces a concrete having about the same long-term strength as straight portland cement-based concretes. However, SCMs sometimes reduce the early strength of the concrete which may be detrimental in certain applications (MCC, 2006, p. 4).

The designations for blended cements vary worldwide, but those currently in use in the U.S. meet either ASTM Standard C595, C 989 or C1157. ASTM Standard C 595 defines several types of blended cements. The main designations include (MCC, 2006, p. 4; von Oss, 2015, p. 16.5)).

- Portland blast furnace slag cement (IS). Contains 25% to 95% GGBFS.
- Portland-pozzolan cement (IP and P). Contains a base of portland or IS cement and 15% to 40% pozzolans.
- Pozzolan-modified portland cement (I(PM)). The base is portland or type IS cement with a pozzolan addition of less than 15%.
- Slag-modified portland cement (I(SM)). Contains less than 25% GGBFS.
- Slag cement (S). GGBFS content of 70% or more. Type S can be blended with portland cement to make concrete or with lime for mortars. The latter combination would make the final cement a pozzolan-lime cement.
- Portland limestone cement (IL). Allows for ground limestone greater than 5% by weight but not more than 15%.
- Ternary blended cement (IT). Allows incorporation of any two of GGBFS, pozzolans, or ground limestone with mass limits on additions (limestone not to exceed 15%).

The most common blended cements available are Types IP and IS. SCM use is increasing, so blended cements are designated using a performance based standard (under ASTM C1157) instead of the composition based standard (ASTM C150)(van Oss, 2005, p. 9). They may be designated as air-entraining, moderate sulfate resistant, or with moderate or low heat of hydration. The following types are recognized:

- Type GU-blended hydraulic cement for general construction (equivalent to type I)
- Type HE-high-early-strength cement (equivalent to type III)
- Type MS-moderate sulfate resistant cement (equivalent to type II)
- Type HS-high sulfate resistant cement (equivalent to type V)
- Type MH-moderate heat of hydration cement (equivalent to type II)
- Type LH-low heat of hydration cement (equivalent to type IV).

These cements can also be designated for low reactivity (option R) with alkali-reactive aggregates. The manufacturer can optimize ingredients, such as pozzolans and slags, to optimize for particular concrete properties.

#### **Pozzolans and Supplementary Cementitious Materials**

Pozzolans and supplementary cementitious materials (SCMs) often are used as a cement replacement or as an enhancement in concrete. By replacing a portion of the cement, the cost of the cement is reduced. Also, offsetting the use of portland cement by using mineral admixtures can save energy and lower  $CO_2$  emissions from cement plants. Artificial pozzolans typically are more environmentally advantageous than natural pozzolans because artificial pozzolans are the waste or byproduct of an ongoing industrial process. It takes energy to mine and process natural pozzolans, potentially adding more  $CO_2$  to the environment. Pozzolans and SCMs may be added to clinker during the final grind phase in the manufacture of cement (Fig. 22) or added to finished cement during construction before adding water and other aggregates to the concrete mix.

Pozzolans are either natural or artificial depending on their provenance. Artificial pozzolans are mostly derived from by product materials of industrial processes. They include silica fume, fly ash, and rice hull ash. SCMs in current use include both GGBFS and high-Ca fly ash which also are by products of industrial processes. Natural pozzolans are either raw or calcined materials from naturally occurring mineral deposits. These all are described below because they all must be considered in the determination of the market value for the potential natural pozzolan commodity present on the Capital MC, except rice hull ash. Rice hull ash sees little use in the U.S. and will be referred only generally (Hoffman, 2006, p. 1164).

Physical and chemical properties of an SCM or pozzolan determines its physical properties and cementitious properties. Pozzolans and SCMs react with the Ca(OH)<sub>2</sub> liberated as concrete hardens, forming compounds with cementitious properties, which makes these materials attractive partial substitutes for portland cement in concrete applications or interground with portland cement clinker to create blended cements. Pozzolans also can counteract the negative effects of undesirable aggregates used in concretes and help to create a concrete highly resistant to penetration and corrosion (Hoffman, 2006, p. 1161). In general, incorporation of a pozzolan or SCM with portland cement improves the resistance of the concrete to chemical attack, reduces

the concrete's porosity, reduces the heat of hydration of the cement, potentially improves the flowability of concrete, and produces a concrete having about the same long-term strength as straight portland cement-based concretes. Some physical and chemical properties of pozzolans and SCMs are summarized in Table 6.

Table 6. Physical and chemical properties of pozzolans and SCMs. Table adopted from Hoffman (2006, p. 1162).

| Properties | Silica Fume  | Ground, Granulated<br>Blast Furnace Slag<br>(GGBFS) | Fly Ash (Class C<br>and Class F)   | Calcined Clay, Shale  | Diatomite   | Rice Hull Ash  |
|------------|--|---|------------------------------------|---|---|--|
| Physical   | Very fine, tiny spheres<br>(0.1 µm), high surface<br>area—acts as filler | Angular, ground to<br><45 µm                        | Fine-grained,<br>spherical, <45 µm | <45 µm rough texture<br>because of grinding                     | Very fine-grained (1 µm).<br>Porous skeletal remains<br>of single-cell plants | Highly cellular,<br>creating large surface<br>area, >45 µm |
| Chemical   | Amorphous silica   | Silicate glass, high<br>in calcium                  | Aluminosilicate                    | Aluminosilicate glass;<br>may contain quartz,<br>feldspar, mica | Amorphous silica  | Pure silica,<br>noncrystalline                             |

The range of reactivity and specific properties dictates usage in the cement and concrete industries. Reactivity can vary depending on the type and extent of processing that either natural or artificial pozzolans undergo. Most natural rock material used as pozzolans undergo grinding or calcination to improve their reactivity, and the percentage of amorphous material in the pozzolan often determines the reactivity of the natural pozzolan (Hoffman, 2006, p. 1162). Table 7 generally illustrates some of the differences and classification based on reactivity.

Table 7. Natural and artificial pozzolans and SCMs classified by reactivity. Table adopted from Hoffman (2006, p. 1162).

| Degree of Reactivity        | Material   |  |  |
|-----------------------------|--|--|--|
| Cementitious and pozzolanic | GGBFS (cementitious)   |  |  |
|                             | High-calcium fly ash (cementitious and<br>pozzolanic)                |  |  |
| Highly active pozzolans     | Silica fume  |  |  |
|                             | Rice hull (or husk) ash from electrical generation                   |  |  |
| Normal pozzolans            | Low-calcium fly ash  |  |  |
|                             | Natural pozzolans—clay, shale,<br>diatomaceous earth, opaline cherts |  |  |
| Weak to very weak pozzolans | Slowly cooled blast furnace slag                                     |  |  |
|                             | Bottom ash   |  |  |
|                             | Boiler slag  |  |  |
|                             | Field burnt rice hull ash  |  |  |

### Silica Fume

Silica fume is a by-product of producing a silicon metal or ferrosilicon alloys by reduction of high-purity quartz with coal or coke and wood chips in an electric arc furnace. The silica fume is condensed from gases from the furnace and collected in bag house filters. Depending on the
process, the silica fume is 94-98% silicon dioxide from silicon production and 85-90% silicon dioxide from ferrosilicon production in amorphous form. Silica fume is a fine powder of glassy spherical particles in the size range of 0.1-0.2  $\mu$ m with surface areas of 20-23 m<sup>2</sup> / g, compared to fly ash which is typically < 45  $\mu$ m in diameter. The chemical composition, size, and surface area of these particles create a very reactive pozzolanic material. Silica fume is highly reactive and results in much higher strength concrete in the same time as portland cement and exceeds the norm in three days. Workability is the homogeneity and ease with which concrete can be mixed, transported, compacted, and finished. The workability of concrete is reduced with silica fume, because of its highly reactive nature (Hoffman, 2006, p. 1169).

Silica fume creates a high-compressive strength product that is very durable and can reduce the amount of reinforcing steel required in concrete applications (Hoffman, 2006, p. 1165). It produces a cement with very low density (specific gravity about 2.22 average) compared to straight portland cement (specific gravity about 3.15 average) (MCC, 2006, p. 8; Wikipedia, https://en.wikipedia.org/wiki/Cement, retrieved January 27, 2017). Products include a powder form, a densified form, a slurry form with water, or a pellet fine powder. It is a value added product for making high strength concrete for high rises, parking structures, bridge decks, and girders. It also is used in shotcrete mixtures, grouts, concrete blocks, and bricks (Hoffman, 2006, p. 1165).

Use of silica fume is limited because only a few companies supply U.S. silica fume. Lack of availability of silica fume drives up the price, so the cost of the silica fume and finished concrete is higher. Thus, silica fume is used where cost is not a consideration or when very high compressive strength and increased resistance to sulfate attack are required in the concrete application (Hoffman, 2006, p. 1164). Physical and chemical requirements for use of silica fume as a mineral admixture in concrete is outlined in ASTM C1240 (Hoffman, 2006, p. 1164).

#### **Ground Granulated Blast Furnace Slag**

Slag is a byproduct in the production of pig iron (an intermediate, high-carbon iron used in the production of steel). It is produced from a high temperature reaction with carbon-reducing agents and fluxes. The impurities of the iron ores and fluxing agents combine to form a liquid silicate melt, slag, that floats on top of the liquid crude iron. The slag is removed or tapped from the blast furnaces separately and quickly quenched. The slag is quenched to create amorphous (glassy) sand sized particles, which is granulated blast furnace slag. Grinding this granulated slag increases the surface area and the reactivity of the GGBFS product (Hoffman, 2006, p. 1165).

GGBFS typically is composed of silicon dioxide (33-36%), calcium oxide (37-40%), aluminum oxide (7-9%), iron oxide (1-10%), and magnesium oxide (periclase; 10-11%). Slag is closest to the composition of portland cement of the pozzolanic byproducts; however, the slag has a higher silica and lower calcium content. The quality of the slag is determined by the quenching method. If quenched with water in a granulator and ground, it makes GGBFS, which is used in high strength concrete. If cooled with water or steam to form pellitized slag, it is ground with portland cement and typically used as a lightweight aggregate (Hoffman, 2006, p. 1166). Slag cement has a lower density than straight portland cement (slag cement average specific gravity about 2.94) (Wikipedia, https://en.wikipedia.org/wiki/Cement, retrieved January 27, 2017).

Slag can replace 10-80% of portland cement in concrete and is used in manufactured products like block, segmental retaining wall units, and pavers. Mixed with hydrated lime, GGBFS can be used in flowable backfills. Specialized concretes can used a combination of GGBFS, fly ash, and silica fume. GGBFS is valued as an admixture in cement for its light color, resulting in light colored concrete. Adding GGBFS to a cement mix gives the concrete greater resistance to sulfate an alkali-silica attack, increased workability while pouring concrete and durability of the finished product (Hoffman, 2006, p. 1166). Physical and chemical requirements for GGBFS are provided in ASTM C989 (Hoffman, 2006, p. 1166).

### Fly Ash

Fly ash is a coal combustion byproduct of electrical generation from coal burning power plants or other types of industrial plants using coal as a fuel. Coals typically have different types of clay, quartz, and feldspar impurities depending on depositional environment. These inorganic materials become molten and remain in the combustion chamber as slag on the boiler tubes to be carried away by the flue gas stream as fly ash, or falls through the bottom of the boiler as bottom ash. The composition of fly ash is dependent on the coal feed and the efficiency of the combustion process. Most fly ash particles are spherical, glassy, < 45  $\mu$ m in diameter, and possess pozzolanic properties (Hoffman, 2006, p. 1162).

Pollution control devices collect fly ash from the flue gas stream coming from the combustion chambers. Electrostatic precipitators collect the coarse ash (> 45  $\mu$ m) first, and mechanical precipitators like bag houses, cyclones, or venturi scrubbers capture the rest. The volume produced depends on types of burners and precipitators and the composition of the coal. Fly ash can be captured by size or sent through classification for consistent grain size. The fly ash is then desulferized to remove sulfur compounds. Physical and chemical requirements for fly ash used as a pozzolan are outlined in ASTM C618. Generally, sub-bituminous or lignite coal produces class C fly ash (a low silica class), and bituminous coals result in class F, but there are exceptions (Hoffman, 2006, p. 1167). Specifications for class C and class F fly ash are shown in Table 8.

Concrete is the major use of fly ash. Class F is used to prevent alkali-silica reaction (ASR) in concrete and is preferred in many southwestern states where the aggregate tends to have reactive material. Light colored concrete is desirable in some markets, particularly California. A low percentage of LOI results in a light colored fly ash. A low LOI also is desirable in air-entrainment admixtures used to counteract freeze-thaw cracking. The type and amount of unburned carbon material can be detrimental to these admixtures. The percentage of LOI can also affect the amount of water to create the needed consistency of the concrete (Hoffman, 2006, p. 1169). Adding fly ash to a concrete mix at 15-25% by weight is common practice.

Fly ash works to reduce the weight of concrete. The average specific gravity of cement with class F fly ash is about 2.38 and with class C about 2.65 compared to a specific gravity of straight portland cement of about 3.15 (Wikipedia, https://en.wikipedia.org/wiki/Cement, retrieved January 27, 2017).

High calcium fly ash (class C) combined with lime improves soils for roadway construction. Fly ash can be mixed with recycled pavement to create a new base course, reducing the need for additional aggregate. Roller compacted concrete (RCC), a very stiff concrete rolled out with

Table 8. Physical and chemical requirements for fly ash and natural pozzolans defined in ASTM C618. Moisture content is a measure of the free water in the material. Loss on ignition LOI) is a measure of water tied up in crystalline structures and of unburned carbon. Uniformity requirements are optional. Table adopted from Hoffman (2006, p. 1167)(Errata note - SAI with portland cement at 28 days minimum % of control is 75 for class N pozzolan and not 77).

|  | Class N | Class F | Class C |
|--|---------|---------|---------|
| Chemical Requirements  |         |         |         |
| (SiO2+Al2O3+Fe2O3), minimum %  | 70.0    | 70.0    | 50.0    |
| SO3, maximum %   | 4.0     | 5.0     | 5.0     |
| Moisture content, maximum %  | 3.0     | 3.0     | 3.0     |
| LOI, maximum %   | 10.0    | 6.0     | 6.0     |
| Optional chemical requirements:  |         |         |         |
| Available alkalies, as Na2O,<br>maximum %  | 1.5     | 1.5     | 1.5     |
| Physical Requirements  |         |         |         |
| Fineness: Amount retained when wet-sieved<br>on 45-µm (325) sieve, maximum %     | 34      | 34      | 34      |
| SAI:*  |         |         |         |
| With portland cement at 7 days,<br>minimum, % of control                         | 75      | 75      | 75      |
| With portland cement at 28 days,<br>minimum % of control                         | 77      | 75      | 75      |
| Water requirement, maximum % of control  | 115     | 105     | 105     |
| Soundness: Autoclave expansion or<br>contraction, maximum %                      | 0.8     | 0.8     | 0.8     |
| Uniformity: <sup>†</sup>   |         |         |         |
| Density, maximum variation from<br>average %                                     | 5       | 5       | 5       |
| Percent retained on 325 sieve, maximum variation, percentage points from average | 5       | 5       | 5       |

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\* The SAI comes from a control mixture of portland cement mortar and a test mixture of portland cement and test sample in accordance with ASTM C311-02 (2003a). SAI with portland cement is a measure of reactivity with a given cement and can vary as to the source of both the fly ash or natural pozzolan and the cement.

† The density and fineness of individual samples must not vary from the average established by the 10 preceding tests, or by all preceding tests if the number is less than 10.

asphalt paving equipment, requires large amounts of fine aggregate than can be satisfied partially with fly ash. Fly ash pozzolanic properties increase the strength of RCC, lowering the cost. Because RCC is often used in large structures such as dams, lowering the heat of hydration by

adding fly ash is very important to minimize cracking. The use of fly ash has greatly diminished the demand for type IV portland cement in large pours.

Fly ash mixed with water and small amounts of sand and portland cement is used for low strength concrete for backfilling trenches. Use of class C fly ash may require less portland cement to form a competent backfill (Hoffman, 2006, p. 1168). Workability is the homogeneity and ease with which concrete can be mixed, transported, compacted, and finished. The sherical shape of the fly ash acts like ball bearings and increases the workability of the concrete, decreasing the need for aggregate fines. Also, the fine particle size in admixtures is advantageous when the aggregate is deficient in sand-sized material. The admixtures act as a filler and are part of the cement paste, reducing the total surface area to be coated with cementitious material. Adding fine  $(1-20 \,\mu\text{m})$  spherical particles such as fly ash can refine the pore structure in the concrete, which reduces the amount of water needed to produce a concrete of certain consistency (Hoffman, 2006, p. 1169).

#### Natural Pozzolan - Characteristics and Specifications

Natural pozzolans (NPs) have been used since Roman times for mortars and cements and were widely used in the mid-20th century in the western U.S., especially for massive structures like dams (Tikalsky, 2001, p. 4). Natural pozzolan deposits in the central and western U.S. were extensively studied during the mid-20th century (cf. U.S. BLM, 1966; Weiler, 1966; U.S. Bureau of Mines (USBM), 1969; and Mielenz, 1951). Most of the deposits with potential for natural pozzolans are located in the central and western states including Kansas, New Mexico, Arizona, California, Utah, Nevada, Idaho, and Oregon.

Natural pozzolans are either raw or processed natural materials including volcanic ash, pumice, pumicite, opaline chert, rhyolitic or dacitic tuff, zeolitic tuff, siliceous shale, diatomite, diatomaceous earth, and some clay (e.g. kaolin) deposits. Arizona and New Mexico host mostly volcanic rock deposits, but California and Nevada both host diatomite and volcanic deposits. A wide array of deposit types can be used if the products from the deposits can meet the specifications for natural pozzolans of ASTM C618 shown in Table 8. All the deposits have in common a high silica and alumina composition and either have to naturally have a significant amorphous component or be processed to achieve a significant amorphous component, essential for the pozzolanic reactivity during hydration. Hoffman (2006, p. 1161) describes three categories of natural pozzolans: volcanic ash or tuff when indurated in which the amorphous constituent is a glass produced by rapid cooling of the magma, those in which the silica is mainly opal or opaline, and diatomaceous earth and some clays and shales. Volcanic tuffs and pumicite used as pozzolans are often referred to as pozzolana in the literature.

Natural pozzolans are used in much the same way as the artificial pozzolans as admixtures in concrete or in blended cements. ASTM specifies in C311 the methods for testing raw and calcined material in portland cement. Standard C618 provides the specifications for use in concrete for natural pozzolans, assigning it to class N, which is similar to class C and F for fly ash (Table 8). Only a few differences exist between natural pozzolans and fly ash class F. The primary differences are that both the maximum LOI, or amount of unburned carbon, is sometimes greater depending on composition and the maximum water requirement sometimes is greater for natural pozzolans because the angular shape of the rock particles typically increases pore space (Hoffman, 2006, p. 1163).

The wide variability in deposits in physical and chemical characteristics means that many of the natural pozzolan materials have to undergo some kind of processing to be able to meet the strict specifications of ASTM C618. Pumice, pumicite, and diatomite typically need to be crushed and milled to meet the fineness requirements and may have to be dried to reduce the moisture content. Siliceous shale and diatomaceous earth with significant clay require calcination at 700-800° C to enhance their pozzolanic characteristics and to destroy existing clay crystal structure to form an amorphous or disordered aluminosilicated structure. Pure clay, e.g., high purity kaolin, may be water processed to remove impurities, lighten color, and control particle size. When the purified material is calcined at 600 to 900° C, water is driven off and an amorphous aluminosilicate is formed. The product is pulverized to 1-2 µm diameter to create a highly reactive pozzonlanic product called metakaolin. Heating increases the pozzolanic reactivity of zeolites also (Hoffman, 2006, p. 1163). (b) (4)

Pozzolanic reactions occur after cement hydration begins when Ca(OH)<sub>2</sub> becomes available. Formation of cementitious compounds by pozzolanic reaction causes pore refinements and reduces microcracking in the transition zone between the cement and aggregate particles. This significantly improves the strength and durability of the concrete. Replacing a portion of the cement with most natural pozzolans retards the rate of hydration and manifests pozzolanic reactions late in the aging process of the concrete. Because of reduced heat of hydration, adding a natural pozzolan lowers the early strength. Strength increases over time and eventually meets, or can exceed, the strength of concrete made with portland cement alone. As a rule, the percent reduction in heat at 7-28 days is about one half the percentage of mineral admixture substitution for portland cement. Reduced heat of hydration is particularly important in massive structures where the temperature increase becomes significant and can lead to cracking because of thermal stresses induced in the hardened portions of the concrete mass. For this reason, the major use of natural pozzolans in the mid-20th century was in mass concrete structures like dams where large pours were required with high risk of chemical cracking from the heat produced from the chemical reactions during hydration (Tikalsky, 2001, p. 4). Adding natural pozzolans slows down the cementation process which reduces the temperature. Many natural pozzolans also improve the workability of the concrete pour, which is beneficial in massive concrete structures.

Natural pozzolans may also be effective in dealing with alkali-silica reactivity in concrete. The presence of reactive material in a concrete aggregate, such as opal, chalcedony, siliceous shale, and schist, causes alkali-silica reactions (ASR) to occur in concrete. ASR occurs when silicate minerals react with alkali metal ions (e.g. Na<sub>2</sub>O and K<sub>2</sub>O) in portland cement paste, forming a gel. With moisture, the gel can swell and expand and crack the concrete around the individual aggregate particles, causing popouts. Most mineral admixtures are effective in controlling ASRs. The available alkalis in the mix is reduced by the amount of admixture added if the added material does not contain soluble alkalis. The size of the particles (1-45  $\mu$ m) improves the packing of the cementitious materials and reduces the permeability of the concrete because of the pozzolanic reaction. This reduces the ion migration and available external moisture in the concrete, increasing the resistance to ASR. Also, the smaller particles of the pozzolans are preferentially attached by alkaline solutions (sacrificial silica), forming a calcium-silicate hydrate (C-S-H) that is more stable than the silica gel (Hoffman, 2006, p. 1170). This protects the aggregate from ASR attack. Some high calcium fly ash (class C) that contains large amounts of

soluble alkali sulfates increases the alkali-silica reactivity. However, class F fly ash, many natural pozzolans, silica fume, and GGBFS are effective in reducing ASR.

In some applications, concrete deteriorates more rapidly because of attack by seawater, acids in the atmosphere, or acid or sulphate-bearing groundwater. Pozzolanic reactions in concrete from natural pozzolans typically reduce the permeability of the concrete and, thus, reduce penetration by harmful chemicals. This enhances the longevity of the concrete application.

Table 9 summarizes some the chemical and physical effects of admixtures of some artificial and natural pozzolans for the performance of concrete. Natural pozzolans provide benefits to the cement and concrete industries very similar to class F fly ash, but they may be blended with class C fly ash or SCMs to enhance concrete in specific applications. Note that Table 9 addresses only calcined shale and diatomite and does not address the various types of natural pozzolan deposits. Properties of materials from deposits like pumice, pumicite, and rhyolitic or dacitic tuff typically improve concrete workability and do not have to be calcined. Also, the pumiceous natural pozzolans are more friendly to air entrainment agents. Air entrainment agents help replace water bubbles in concrete with air bubbles. Water bubbles can freeze in cold climates and cause cracking. When displaced by air with air entrainment agents, cracking is reduced. Fly ash essentially is burned carbon and silica glass, and any unburned carbon (high LOI) can create issues with air entrainment. The natural pumiceous pozzolans do not create air entrainment issues like a high LOI fly ash (b) (4).

| Table 9. | Effects of pozzolans and SCMs on the performance of concrete. | Table adopted from |
|----------|---|--------------------|
| Hoffman  | (2006, p. 1169).  |                    |

| Description                              | cilian rama   | CODEC   | Fly Ash  | Calcined Clay,   | D' 1 - 1   |   |
|--|---|---|--|--|--|---|
| Property                                 | Silica Fume   | GGBFS   | (Class C and Class F)  | Shale  | Diatomite  | Rice Hull Ash                                       |
| Water demand                             | Depends on mixture  | Decreases   | Generally<br>decreases; with<br>higher % LOI and<br>coarse ( >45 µm)<br>particles, increases         | Increases  | Increases because<br>of microporosity                  | Increases   |
| Workability                              | Decreases, becomes<br>sticky  | Improves  | Improves   | Improves   | Unknown  | Improves  |
| Flow of pour                             | Decreases   | Increases   | Increases  | Unknown  | Unknown  | Unknown   |
| Compressive<br>strength                  | High compressive<br>strength attained in<br>same time as<br>portland cement | Lower during first 3–<br>7 days. By 28 days,<br>meets or exceeds<br>strength of portland<br>cement. | Increases slower<br>than normal; with<br>time (+60 days),<br>exceeds strength of<br>portland cement. | Increases with time,<br>slower than<br>portland cement | Increases with time,<br>slower than<br>portland cement | Moderately high,<br>greater than portland<br>cement |
| Durability                               | Increases   | Increases   | Increases  | Increases  | Increases  | Increases   |
| Heat of hydration                        | Accelerates<br>temperature rise in<br>first 72 hours                        | Lower   | Lower, except in<br>high-calcium fly ash   | Lower  | Lower  | Same as portland cement                             |
| Air-entrainment<br>agent                 | Increases demand  | Increase demand   | Higher % LOI,<br>greater demand  | Unknown  | Unknown  | Increases demand                                    |
| ASR resistance                           | Increases   | Increases   | Increases  | Increases  | Increases  | Increases   |
| Sulfate resistance                       | Increases because<br>of refined pore<br>structure                           | Increases   | Increases with<br>Class F fly ash  | Increases  | Increases  | Increases   |
| Bleeding of<br>hydrated lime,<br>Ca(OH)2 | Lower than normal;<br>increases potential<br>for cracking                   | Generally lower   | Generally lower  | Lower than portland cement                             | Lower than portland cement                             | Negligible difference                               |

#### **Testing and Analytical Work for Natural Pozzolans**

Analytical testing for NPs may be very specific to determine whether the NP meets the requirements of a specific application and, thus, may be demanded by the buyer. However, all

NPs have to meet the requirements of ASTM C618 even to be considered a marketable product. Because of stiff competition in the current market, the NP not only must meet the specifications of ASTM C618 (cf. Table 8), but most likely must exceed the requirements. The greatest concerns of potential buyers typically are reactivity in the concrete (whether it reacts the way it is supposed to), and water demand (< 100% of control is desirable) in the concrete mix (b)

Also, buyers desire information about performance of the product and are willing to pay more for consistency in the product because this equates to consistent performance in the concrete mix (b) (4)

. Thus, testing and analyses must address the physical and chemical characteristics of the commodity and its performance in the eventual concrete applications. ASTM C311 provides the procedure for testing to ensure requirements are met for ASTM C618.

Samples are first tested using various methods for whole rock analysis to determine whether the material meets the basic chemical requirement of ASTM C618, i.e., whether the  $SiO_2 + Al_2O_3 + Fe_2O_3$  (SAF) by weight meets or exceeds 70%. This requirement is critical to ensure that the materials has the right chemistry for pozzolanic reaction during hydration. However, the whole rock analyses do not show whether the SAF results from amorphous phases or crystalline phases. Amorphous phases are critical for pozzolanic reaction. Subsequent performance tests under ASTM C311 confirm the reactivity and provide confirmation whether amorphous phases prevail.

Whole rock analyses also provide information for other element requirements for ASTM C618. The SO<sub>3</sub> content of the material must be <4.0% because S may negatively impact the pozzolanic reactions. Also, total available alkalis must be <1.5% to ensure that the material helps alleviate ASR instead of contribute to ASR. This value is not equivalent to the total whole rock weight of the alkali metals but measures those prone to reaction in the mix.

In situ moisture content is measured by heating the sample for a short period of time, measuring the weight, then burning the sample for a longer period of time. The moisture loss from heating the sample (extreme drying) is considered a measure of the free water in the pore space and provides information whether the material would have to be dried before use in a cement blend or concrete admixture. Ignition provides LOI which is a measure of the water tied up in the lattice of crystalline phases and any other burnable substance, e.g., carbon. Fly ash essentially is a burned carbon and silica glass, and if significant carbon remains in the fly ash, it can react like activated carbon and affect air entrainment. (b) (4)

If the

LOI is high from a significant amount of clay in the material, calcination is required.

The NP is then tested using ASTM C311 protocol for density. NP typically is lighter and less dense than portland cement (average specific gravity about 3.15). When NP is blended with cement, the result is a lighter weight concrete.

The material is tested for fineness using a particle size distribution test. This test provides information that helps the NP producer determine the amount of milling that will be necessary to meet ASTM C618 requirements and ensure a small particle size to enhance the pozzolanic reactivity in cement blends.

Soundness is measure using the autoclave expansion test so the material can be tested for excessive expansion or contraction, primarily caused by Mg or lime. Expansion or contraction cannot exceed 0.8% to meet ASTM C618 requirements.

Compressive strength tests are conducted to measure the actual performance of the material. Both seven day and 28 day tests are required to meet the specifications of ASTM C618. These tests are critically important to potential buyers and users of concrete, like departments of transportation, precasters, and ready mix producers (b) (4)

. The material is compared to the compressive strength of pure portland cement using the strength activity index (SAI). The index material is 100%, and the tested materials is reported as a percentage at seven days and 28 days compared to the index. The minimum requirement for a class N pozzolan in 75% after seven days or 28 days (Table 8). Typically class F fly ash is 75-85% index after seven days and 80-90% after 28 days. Metakaolin and premium volcanic NP (high glassy content) typically test as good as fly ash or better, while some lesser quality NP may not test as good (b) (4)

The water demand test provides an estimate of the amount of additional water that will be needed in a concrete mix compared to a straight portland cement control material. It is reported in percent of control and must not exceed more than 115% of control. Water demand in NP typically is higher than fly ash because the particle shape is angular compared to the spherical shape in fly ash. (b) (4)

The ASTM C311 tests typically are followed by a 14-day test according to ASTM C1567 to determine how well the material mitigates against ASR (b) (4)

To be marketable, a NP must pass this test and not contribute to ASR

Mitigation against sulfate attack is measured using ASTM C1012. Sulfate causes expansion and eventual deterioration of the concrete. This test takes from six to 18 months. Materials with high alumina typically don't mitigate sulfate attack as well as those with low alumina (b) (4)









#### Mineral Exploration and Development Work

The Capital MC site has been prospected at least since the late 1890s, because the original placer mining claim was located in 1896. Mining has been conducted in this location since the early 1900s (Arizona Geological Survey, 2015, Rynearson Kirkland Quarry file). The area has been known variously throughout its history as the Arizona Tufa ("Magic Mountain") Property, Rynearson Quarry, Kitty Litter Mine, and Capital Quarry. In 1958, the Rynearson family leased the quarry to Capital Quarries to provide dimension stone for construction of the Arizona State Capital Building (Kirkland Mining Company, 2015, p. 6; Townsend, 1961, p. 29). Stone also was used to construct buildings in Kirkland, Congress, Yarnell and Wickenburg, Arizona. Quarry sites from this operation exist near the southern border of the Capital MC and immediately adjacent to the south boundary on the Homesteak MC (Fig. 19).

In 1979, Kitty Litter Mine began shipping oil absorbent material from the mine at a rate of approximately 1,200 tons of tuff per month (Kirkland Mining Company, 2015). The mine was closed in 1985, and the equipment was removed. The quarry site and a stockpile for the absorbent operation remains open today in the west central part of the Capital MC (cf. disturbed area in Fig. 3 and Fig. 5).

The Kirkland site was idle from 1985 until the recent exploration and evaluation by the Zouvas family and Kirkland. Detailed work and sampling began in 2013. Kirkland filed a mineral material sale application with the BLM on April 21, 2015 (AZA 036775) for production of mineral materials from the stockpile. This application was withdrawn and replaced with a new application July 7, 2015 (Kirkland Mining Company, 2015). That application is pending awaiting the outcome of this investigation.

The site is currently being evaluated as an industrial mineral deposit with emphasis on natural pozzolan. A notice of exploration for bulk sampling and drilling was filed with the BLM on August 11, 2015 (AZA 36808). Bulk sampling, surface outcrop sampling, and drilling and sampling has occurred periodically and is ongoing under this notice of exploration. Core holes were drilled in February and March 2016 (Fig. 19).

#### Mining, Milling, and Related Operations

#### **Mining methods**

Currently, no mining is occurring on the Capital MC, although Kirkland filed a mining plan on July 7, 2015, with BLM under 43 CFR 3600 for an individual sale of mineral materials to be produced from the historic stock pile in the southwest central part of the Capital MC. That plan is pending further evaluation for mining to produce a natural pozzolan product.

#### (b) (4)



The stockpile will be mined in a simple load haul operation using a front loader and trucks. When mining begins at the outcrop, a bull dozer most likely will be used to rip the rock before before removal and crushing. The mineral material mine plan outlines the equipment that will be used:

Caterpillar 988G front-end loader or equivalent for truck loading
water truck for dust control
Caterpillar D6 dozer or equivalent for clearing and grubbing
pick-up truck for employee transport and supervision
Bulk dump trucks as needed for hauling high quality pozzolan (HQP) to customers.

This equipment is reasonable for mining the stockpile; however, a more powerful bull dozer will be needed if the rock needs to be ripped, mostly likely a D10 or D11 equivalent.

Material will be mined at the outcrop with a front end loader and transported to a portable screen and crusher on site. Dump trucks with a 10 cubic yard capacity mostly likely will be used to haul the crushed material to a processing plant, if necessary. The processing plant will be located on private land near Kirkland approximately 1.5 miles away.

The intended mining operations at the Capital MC will be an open pit operation. It will be tantamount to mining an indurated pumice or perlite deposit. Techniques will be similar to an aggregate mine except the material will be slightly harder with higher costs.

#### **Processing methods**

The Kirkland tuff will be marketed as a NP, which means that it will have to be processed to meet the specifications of potential buyers. The material in the stockpile (approximately 48,000 tons; Kirkland Mining Company, 2015) most likely will be loaded and sold without crushing, screening, or milling to buyers who will process the material for NP. Typically, rock from the outcrop will undergo processing to meet the minimum specifications of ASTM C618.





The onsite screening and crushing plant on the Capital MC will be equivalent to a portable plant in a comparable sized aggregate or cinder quarry.

#### **Common Variety Determination**

#### **Potential Deposit Products**

The potential products from the Kirkland tuff on the Capital MC were described above in the Mineral Deposits section. The Kirkland tuff is somewhat unique in that it was used historically as a dimension stone and was prospected and mined as an absorbent. (b) (4)

Some of these uses

may be common variety uses, but this ongoing specification and market exploration by Kirkland most likely will result in a number of commodities that can be produced from the tuff that can be considered marketable commodities that potentially could support an uncommon variety deposit.

However, the currently available data support only a determination whether the deposit can be considered an uncommon variety for natural pozzolan. Thus, the focus of this determination is limited to that question.

#### **Deposit Comparison**

The Kirkland tuff is in the field of volcanic and volcanic derived deposits which are widespread in the western U.S. Deposits of air fall tuff, water lain tuff, pumice, pumicite, cinders, and welded tuff resulted from widespread volcanic activity that started about 65 million years ago and continues today along the Rio Grande rift of New Mexico, near Yellowstone in Wyoming and Idaho, and the Pacific northwest from Mt. Lassen in California to Mt. Rainier in Washington. Relatively recent volcanic activity occurred in both Idaho and northern Arizona. Ash fall from volcanoes drifted eastward and fell in the Great Plains, forming pumicite deposits in Kansas and Nebraska. Rocks in the Tertiary basins of the western U.S. typically record this volcanic activity and contain both fresh water sedimentary rocks and interbedded volcaniclastic deposits. Some of these sedimentary and volcaniclastic deposits have been altered by chemicals in ground water, leading to the formation of extensive clay and zeolite deposits.

Thus, the Kirkland tuff is not unique in terms of provenance for the western U.S.; however, it is unique among the array of volcanic and volcaniclastic deposits because of its lithology.

#### (b) (4)

The Kirkland tuff meets all the requirements for a NP that can be used in the manufacture of cement and concrete. Deposits of siliceous shale, diatomite, diatomaceous earth, opaline chert, clay, pumice, and pumicite also can be used as a NP if they meet the minimum requirements set by industry for a NP. These deposits also are widespread in the western U.S., the presumed potential market area of the NP tuff from the Capital MC. Since NP is an extender for cement and concrete, the Kirkland tuff could be and should be compared generally with aggregates of any kind that extend concrete, especially common light weight aggregates and sand and gravel deposits. It must be compared with true common variety mineral deposits to determine whether it is categorized as another one of them or should be categorized as an uncommon variety deposit because it is highly valued for an intrinsic, unique characteristic some step above the run of the mill common variety deposits.

Under the McClarty guidelines (cf. above section on legal framework), the general deposit comparison should be limited to deposits and deposit commodities that can be used in the same market geographic area. Also, the reason for the comparison is to determine whether the deposit hosts some unique, intrinsic characteristic that sets it apart from widespread deposits of commonly occurring and commonly used materials. Thus, the comparison below is to show where the deposit really falls in relation to the wide array of deposits that produce materials for the cement and concrete industry in the western U.S. Information below includes general information from groups of deposits and specific data from some deposits that produced or continue to produce products related to the cement, concrete, and construction industries. Information was compiled for many deposits in this investigation; however, it is not all reported here. Pertinent information to distinguish the Kirkland tuff is reported, and some specific information for deposits that can compete in the market with the tuff or illustrate differences in characteristics appears in Appendix H.

#### **Descriptions of Other Deposits Generally**

The common variety deposits in the market area are widespread and include sand, gravel, cinders, diatomaceous earth, shale, clay, impure limestone, crushed stone, and the like (cf. Fig. 18 for locations of some Arizona deposits in proximity to the Kirkland deposit). Most of these deposits produce only a few commodities (e.g. construction and asphalt gravel, aggregate for concrete, landscape material, cinders for road maintenance, etc.) instead of a wide array of products that can be used in many industrial applications. The deposit products typically are low value products which limits their use to a local or smaller regional market. Simply, the cost of transportation overwhelms the value of the product, and producers are forced to sell products locally. The supply at any distance is met by another deposit of widespread occurrence closer to the point of use.





Another example of common variety type deposits are the cinder deposits near Flagstaff, Arizona. Similar types of deposits occur in New Mexico and Idaho. These deposits produce only cinders. The cinders may be used for wintertime road maintenance, landscape materials, outdoor grills, or aggregates in construction block. The material is mined with a front end loader, crushed, and screened. (b) (4)

(b) (4) he retail price reflects both distant transportation costs and high demand for ground cover in lieu of using excessive water for lawns (now common practice in the southwestern U.S.). (b) (4)

Superlite Block, Inc., Flagstaff, Arizona, has mined cinders from the Darling Mine site near Winona, Arizona, east of Flagstaff since 1959

(http://www.modernphoenix.net/superlitecapital.htm, retrieved February 13, 2017). It uses the cinders to manufacture construction block that is used widely in Arizona and adjoining states.



Pumice and tuff deposits are widespread in New Mexico, Arizona, Utah, Idaho, Oregon, Washington, Nevada, and California. Pumice is used in a wide array of applications as an agricultural and horticultural soil amendment, light weight aggregate, abrasive, landscape material, filtration aid, filler, roofing material, and as an insulation material, among others (Presley, 2006, p. 748 and 749). These deposits compete in a variety of markets. The deposits

that can produce a variety of products in markets that come and go because of changing supply and demand stand the best chance of long term production and competing with similar deposits that are developed in those markets (b) (4)

Pumice deposits have been produced as both common and uncommon variety deposits (e.g., White Vulcan Mine, Table 10), depending on the industrial use and market forces. These deposits typically are versatile in the products that can be produced, and some special application products can be sold in regional or international markets. Most of them are mined in open pit or quarry operations with simple mining (some blast, some not), crushing, and screening operations.

| (b) (4)                                     |   |        |
|---|---|--------|
|   | (b) (4)                                   |        |
|   | Some deposits have to be dried to be proc | cessed |
| and meet the ASTM C618 specifications which | ch adds to the production costs. (b) (4)  |        |
|   |   |        |
|   |   |        |

A number of

(b) (4)

deposits of pumice occur in Nevada and California that potentially meet the requirements of ASTM C618 (cf. Nevada-California compilation, Appendix H).



A similar situation exists in Arizona. Pumice mines that once supplied light weight aggregate are no longer operating (e.g. White Vulcan Mine, Table 10). In Arizona, bottom ash from coal power plants is used as a substitute to meet the demand for light weight aggregate. (b) (4)

| Deposit Name           | Approximate<br>Location  | Producer and<br>Production Status                    | Deposit Type &<br>Characteristics | Pertinent Products   | Product Price<br>(f.o.b. mine or<br>plant tailgate; per<br>short ton) | Notes  |
|------------------------|--|--|-----------------------------------|--|---|--|
| Naturalite Mine        | Secs. 8,9, 16, 17, T.<br>17 N., R. 22 E., Mt.<br>Diablo B&M,<br>Storey Co., NV     | Nevada Cement<br>Natural Pozzolan -<br>Producing     | Pumiceous rhyolite;<br>pumicite   | Class N natural<br>pozzolan  | (b) (4)   | Potential uncommon<br>variety  |
| Mustache Mine          | Secs. 27, 28, 34, T.<br>20 N., R. 24 E., Mt.<br>Diablo B&M, Lyon<br>Co., NV        | Nevada Cement<br>Natural Pozzolan -<br>not producing | Diatomite                         | Unknown but<br>probably class N<br>pozzolan                          |   | Common variety<br>determination<br>pending; probably<br>require calcination  |
| Rocky Mountain<br>Mine | Sec. 33, et al. ,T. 21<br>N., R. 7 E.,<br>NMPB&M, Rio<br>Arriba Co., New<br>Mexico | CR Minerals<br>Company, LLC -<br>producing           | Pumice; pumicite                  | Class N natural<br>pozzolan; light<br>weight aggregate;<br>landscape |   | Operated partially<br>under mineral<br>material contract<br>from BLM; no<br>common variety<br>determination<br>completed |
| Wright Creek Mine      | Sec. 8, T. 12 S., R.<br>35 E., Boise B&M,<br>Oneida Co., Idaho                     | Hess Pumice -<br>producing                           | Pumice                            | Class N pozzolan   |   | International<br>market; also mines<br>nearby perlite;   |
| White Vulcan Mine      | Sec. 19, T. 23 N., R.<br>8 E., Gila & Salt<br>River B&M,<br>Coconino Co., AZ       | Formerly Arizona<br>Tufflite - not<br>producing      | Pumice                            | Laundry grade<br>pumice; light weight<br>aggregate                   |   | Subject to Multiple<br>Use decision; no<br>longer uncommon<br>variety if it was<br>producing                             |
| Hazen Mine             | Secs. 6, 9, T. 19 N.,<br>R. 26 E., Mt. Diablo<br>B&M, Churchill<br>Co., NV         | EP Minerals -<br>producing                           | Diatomaceous earth                | DE for absorbent,<br>filler, filtration                              |   | Unknown whether<br>common or<br>uncommon variety   |
| Helmer-Bovill Mine     | 46.8425 N. Lat.,<br>116.4272 W. Long.,<br>Latah Co., ID                            | I-Minerals, Inc -<br>under development               | Kaolin                            | Metakaolin   |   | Calcination<br>required; high end<br>SCM   |
|                        |  |  |                                   |  |   |  |

| Table 10. | Comparable de | posit information. | Tabulated dep | posits referred i | n text and Appendix H. |
|-----------|---------------|--------------------|---------------|-------------------|------------------------|
|           |               |                    |               |                   |                        |

| Deposit Name             | Approximate<br>Location                                  | Producer and<br>Production Status                 | Deposit Type &<br>Characteristics | Pertinent Products                                 | Product Price<br>(f.o.b. mine or<br>plant tailgate; per<br>short ton) | Notes                                      |
|--------------------------|--|---|-----------------------------------|--|---|--|
| Lassenite Mine           | Sec. 11, T. 23 N.,R.<br>11 E., Mt Diablo,                | Geofortis Mining<br>and Minerals, LLC -           | Tuffaceous siltstone:             | Potential class N<br>natural pozzolan              | (h) (4)   | Calcination<br>probably not                |
|                          | Lassen Co., CA   | producing   | diatomaceous tuff                 | r r  |   | required                                   |
| Antelope Creek<br>Quarry | Sec. 33, T. 9 N., R.<br>5 W., G&SRM,<br>Yavapai Co., AZ  | Schuck<br>Development -<br>producing              | Gravel, sand                      | Construction Sand<br>and Gravel<br>(ABC);Aggregate |   | Common variety deposit                     |
| Kirkland Quarry          | Sec. 28, T. 13 N., R.<br>4 W., G&SRM,<br>Yavapai Co., AZ | Kirkland Mining<br>Company - under<br>development | Rhyodacitic tuff                  | Class N pozzolan                                   |   | Common variety<br>determination<br>pending |
|                          |  |   |                                   |  |   |  |

Pumice and pumicite deposits typically compete with deposits of other materials that may be used for substitutes in industrial applications. For example, both pumice and diatomaceous earth compete in the filtration markets. If the material meets the industrial ASTM standards and specifications required by a specific customer for a specific applications, it is a valuable commodity. Both pumice and diatomite compete in the NP market in a similar way. They are geologically different materials, but both have the characteristics that allow them to meet the NP requirements (cf. Nevada-California compilation, Appendix H). Artificial substitutes (e.g., fly ash in the pozzolan market) may compete with the natural deposit products. Innovative marketing and salesmanship can dictate contracts that can be obtained for products from a specific deposit and how well the natural materials compete with substitutes.

Diatomite and diatomaceous earth deposits also are widespread in the western U.S. but most prevalent in Nevada and California (Appendix H, Nevada-California compilation). Some of these deposits also are versatile in physical and chemical characteristics, and products can compete in a variety of markets. These types of deposits have been determined both common and uncommon variety deposits depending on the specific uses and value in markets. The opaline and amorphous nature of the diatoms that comprise these deposits allow them to meet the requirements for a class N NP, and the material can react similarly to the amorphous silica in the form of natural glass from a pumice deposit. (b) (4)



Some deposits (b) (4) may have to be calcined to be useful as a pozzolan to transform a minor clay component. Others like siliceous shale and kaolin may have to be calcined to transform major components or the entire rock. Complete transformation of the

natural physical and chemical character of the rock to make a new product typically is considered a manufacturing (value added) process rather than a beneficiation or mineral processing step. Deposits that require only some calcination for purification without changing the entire character of the natural, intrinsic characteristic and have a distinct and special value in the marketplace may be considered an uncommon variety. To evaluate those that require extreme calcination, the value comparison must be based on the value given the deposit by an intrinsic characteristic, not on the value of a manufactured material. <sup>(b)</sup> <sup>(4)</sup>

It will require only simple beneficiation to achieve the optimum particle size.

Thus, the Kirkland tuff definitely is among the class of deposits with physical and chemical characteristics that will allow it to compete in a number of industrial application markets. (b) (4)

The physical and chemical data obtained for this report and testing for other applications indicate that the Kirkland deposit is a tuff but can be used like a more pure pumice in many applications. It has intrinsic characteristics that allow it to be as reactive or more reactive as a pozzolan than pumice, diatomite, or diatomaceous earth in cement and concrete. It properly rests in the field of versatile deposits with a wide array of potential industrial commodities. It is a unique tuff that physically and chemically is very similar to a more pure pumice deposit.

The Kirkland tuff meets all the specifications for a class N NP, and testing data collected to date indicate it will perform as well or better than currently developed NP deposits. Thus, it properly resides is in a class of deposits above the class of typical common variety deposits with products used only as extenders in construction materials and concrete. It clearly is a cement and concrete enhancer in addition to being a cement and concrete extender. It is among the field of the types of deposits that have been determined to be uncommon variety deposits based on value of specific products in the marketplace.

#### **Identification of Competing Deposits**

Only three deposits in the western U.S. currently produce a significant volume of NP, the Hess Wright Creek Mine in Idaho, the Nevada Cement Naturalite Mine in Nevada, and the CR Minerals Rocky Mountain Mine in New Mexico (Table 10). Each of these deposits is similar in their physical and chemical characteristics but unique in the way each is used as a NP for cement blends and concrete admixtures. The fact that they are producing places them in the elite of NP deposits because they are versatile enough to have entered a market saturated so long by class F fly ash. Sales from each of the three deposits is growing as the demand for specialty blend cement increases and the supply of class F fly ash fails to meet the demand.

The Kirkland tuff also will compete for market position with other potential NP deposits in the western U.S. Deposits of diatomite, diatomaceous earth, siliceous shale, opaline chert, some clays, zeolitic tuffs, and rhyolitic to dacitic tuffs may have potential as NP and be considered for development as the market for NP expands (e.g., deposits shown in the Nevada-California

compilation, Appendix H). All of these have the potential to be uncommon variety deposits if their unique, intrinsic characteristics is reflected in a distinct and special value in the marketplace.

The Kirkland tuff also will compete in the market with artificial SCMs including fly ash, GGBFS, silica fume, and metakaolin. Market prices still are driven by these materials because the supply is still meeting most of the demand, and the cement and concrete producers still rely on familiar pozzolans.

#### **Pozzolan Market Overview**

The market for pozzolans and SCMs obviously is intricately intertwined with the cement and concrete markets. Trends in these markets follows closely trends in the construction industry which mirrors the general economy.

#### **Cement and Concrete Markets**

Currently, the cement market still is in a state of rebound from the world-wide economic downturn of 2008. Since the downturn, the annual production of cement has been increasing erratically but, nevertheless, increasing (Table 11). U.S. production in 2016 was approximately 82.9 million metric tons of portland cement and approximately 2.5 million metric tons of masonry cement. Of this, approximately 70% of sales went to ready-mixed producers, 10% to concrete product manufacturers, 9% to contractors mostly for road paving, 4% to oil and gas well drilling, 4% to building material manufacturers, and 3% to others (van Oss, 2017b, p. 44). Lower prices for oil and gas with attendant reduction in drilling has slowed the growth in the cement industry during the last two years in the midcontinent and western states.

Table 11. Salient statistics for cement in the United States. Table adopted from van Oss (2017b, p. 44). Footnotes: <sup>e</sup>Estimated; <sup>1</sup> Portland plus masonry cement unless otherwise noted, excludes Puerto Rico; <sup>2</sup> Includes cement made from imported clinker; <sup>3</sup> Production of cement (including from imported clinker) + imports (excluding clinker) - exports + adjustments for stock changes; <sup>4</sup> Defined as imports (cement and clinker) - exports; <sup>5</sup> Hydraulic cement and clinker.

| Salient Statistics—United States:1                  | 2012   | 2013   | 2014   | 2015    | 2016 <sup>e</sup> |
|---|--------|--------|--------|---------|-------------------|
| Production:   |        |        |        |         |                   |
| Portland and masonry cement <sup>2</sup>            | 74,151 | 76,804 | 82,600 | *83,700 | 85,400            |
| Clinker   | 67,173 | 69,420 | 74,372 | °76,000 | 77,000            |
| Shipments to final customers, includes exports      | 79,951 | 83,187 | 90,070 | 93,340  | 96,300            |
| Imports of hydraulic cement for consumption         | 6,107  | 6,289  | 7,584  | 10,376  | 12,000            |
| Imports of clinker for consumption                  | 786    | 806    | 720    | 942     | 1,700             |
| Exports of hydraulic cement and clinker             | 1,749  | 1,670  | 1,397  | 1,294   | 1,100             |
| Consumption, apparent <sup>3</sup>                  | 77,900 | 81,800 | 89,200 | e93,300 | 96,200            |
| Price, average mill value, dollars per ton          | 89.50  | 95.00  | 100.50 | e105.50 | 111.00            |
| Stocks, cement, yearend                             | 6,900  | 6,570  | 6,140  | °5,600  | 5,700             |
| Employment, mine and mill, number <sup>e</sup>      | 10,500 | 10,300 | 10,000 | 10,000  | 9,500             |
| Net import reliance <sup>4</sup> as a percentage of |        |        |        |         |                   |
| apparent consumption                                | 7      | 7      | 8      | 11      | 13                |

Although the percentages change annually, the production of concrete in Colorado, Wyoming, Arizona, New Mexico, Utah, Nevada, Idaho, Montana, Washington, Oregon, and California accounted for approximately 26% of the concrete produced in the U.S. (MCC, 2006, p. 15). For a typical concrete mix, one metric ton (1.102 short tons) of cement (powder) will yield about

3.4 to 3.8 cubic meters (4.45 to 4.97 cubic yards) of concrete weighing about 7 to 9 metric tons (7.7 to 9.9 short tons)(i.e., the density is typically in the range of about 2.2 to 2.4 metric tons per cubic meter). Although aggregates make up the bulk of the mix, it is the hardened cement paste that binds the aggregates together and contributes virtually all of the strength of the concrete, with the aggregates serving largely as low cost fillers. The strengths of the cement paste is determined by both the quality and type of the cement and the water-to- cement ratio (van Oss, 2005).

#### Market Area

Markets for natural pozzolans are in blended cements, intergrinding the pozzolan with the portland cement clinker, and as a mineral admixture for concrete. Natural pozzolans close to the job site and that do not require calcining are the most attractive. Those that do not require calcination are attractive beyond a local market. Calcined clay and shale tend to be marketed for blended cements and are used directly by the cement companies. Companies mining and marketing diatomite. pumice, and pumicites as pozzolans often sell these materials as mineral admixtures (Hoffman, 2006, p. 1163); however, as the cement and concrete industries learn more about available natural pozzolans, these trends are changing.

Data are not available currently for precise volumes of cement produced in that region, but the U.S. Geological Survey has published data from 2013 (Table 12). Production can fluctuate annually, but these data show that in 2013, about 23% of the portland cement produced in the U.S. was produced in 26 plants in Colorado, Wyoming, Arizona, New Mexico, Utah, Nevada, Idaho, Montana, Washington, Oregon, and California. Pozzolan demand in the eastern U.S. essentially is met by closer availability of fly ash from power plants, GGBFS from the iron industry, and metakaolin from Georgia. Fly ash from Texas is dwindling, but so far the demand is met with fly ash and metakaolin. (b) (4)

#### Table 12. Cement production in the U.S. by district. Table adopted from van Oss (2015, p. 16.10). PORTLAND AND BLENDED CEMENT PRODUCTION, CAPACITY, AND STOCKS IN THE UNITED STATES, BY DISTRICT<sup>1</sup>

| 2012                                       |           |                         |             |                       | 2013                |           |                         |           |                       |                     |
|--|-----------|-------------------------|-------------|-----------------------|---------------------|-----------|-------------------------|-----------|-----------------------|---------------------|
|  | Number    |                         | Grinding    | Percentage            | Yearend             | Number    |                         | Grinding  | Percentage            | Yearend             |
| District <sup>2</sup>                      | of plants | Production <sup>3</sup> | capacity4   | utilized <sup>5</sup> | stocks <sup>6</sup> | of plants | Production <sup>3</sup> | capacity4 | utilized <sup>5</sup> | stocks <sup>6</sup> |
| Maine and New York                         | 4         | 2,004                   | 3,604       | 55.6                  | 224                 | 4         | 1,719                   | 3,604     | 47.7                  | 200                 |
| Pennsylvania                               | 8         | 3,360                   | 6,010       | 55.9                  | 328                 | 8         | 3,619                   | 6,079     | 59.5                  | 271 7               |
| Illinois                                   | 3         | 1,149                   | 2,755       | 41.7                  | 283                 | 3         | 1,104                   | 2,532     | 43.6                  | 194                 |
| Indiana                                    | 4         | 2,393                   | 3,745       | 63.9                  | 208                 | 4         | 2,284                   | 3,745     | 61.0                  | 210                 |
| Michigan                                   | 4         | 3,891                   | 5,515       | 70.5                  | 527                 | 3         | 3,855                   | 5,224     | 73.8                  | 581                 |
| Ohio                                       | 2         | 797                     | 1,188       | 67.1                  | 47                  | 2         | 829                     | 1,207     | 68.7                  | 49                  |
| Iowa, Nebraska, South Dakota               | 5         | 3,140                   | 5,824       | 53.9                  | 407                 | 5         | 3,176                   | 5,932     | 53.6                  | 416                 |
| Kansas                                     | 3         | 1,732                   | 3,348       | 51.7                  | 236                 | 2         | 1,776                   | 3,172     | 56.0                  | 213                 |
| Missouri                                   | 5         | 7,951                   | 10,929      | 72.8                  | 510 7               | 5         | 8,223                   | 10,929    | 75.2                  | 537 7               |
| Florida                                    | 8         | 3,786 8                 | 10,000 r,7  | 37.8 7                | 264                 | 8         | 4,680                   | 9,620 7   | 48.6 7                | 279                 |
| Georgia, Maryland, Virginia, West Virginia | 6         | 5,280                   | 8,216       | 64.3                  | 413 7               | 6         | 5,417                   | 7,360 7   | 73.6 7                | 362                 |
| South Carolina                             | 3         | 2,766                   | 5,085       | 54.4                  | 133                 | 3         | 2,776                   | 5,085     | 54.6                  | 142                 |
| Alabama, Kentucky, Tennessee               | 8         | 5,669                   | 10,141      | 55.9                  | 613                 | 8         | 5,760                   | 10,141    | 56.8                  | 582                 |
| Arkansas and Oklahoma                      | 4         | 2,057                   | 3,655       | 56.3                  | 179                 | 4         | 2,044                   | 3,729     | 54.8                  | 181                 |
| Texas, northern                            | 6         | 4,527                   | 7,583       | 59.7                  | 250                 | 6         | 4,453                   | 7,674     | 58.0                  | 266                 |
| Texas, southern                            | 6         | 5,472                   | 6,529       | 83.8                  | 261                 | 6         | 5,662                   | 7,708     | 73.5                  | 277                 |
| Arizona and New Mexico                     | 4         | 1,540                   | 3,715       | 41.4                  | 112                 | 4         | 1,784                   | 3,715     | 48.0                  | 120                 |
| Colorado and Wyoming                       | 4         | 2,875                   | 4,517       | 63.6                  | 191                 | 4         | 2,897                   | 4,889     | 59.3                  | 228                 |
| Idaho, Montana, Nevada, Utah               | 6         | 2,439                   | 3,729       | 65.4                  | 228                 | 5         | 2,099                   | 3,250     | 64.6                  | 208                 |
| Alaska and Hawaii                          |           | -                       |             |                       | 72                  |           |                         |           |                       | 68                  |
| California                                 | 9         | 8,402                   | 11,989      | 70.1                  | 477                 | 9         | 9,264                   | 12,080    | 76.7                  | 402                 |
| Oregon and Washington                      | 4         | 993                     | 2,399       | 41.4                  | 238                 | 4         | 1,266                   | 2,399     | 52.8                  | 201 7               |
| Importers <sup>9</sup>                     |           |                         |             |                       | 285 7               |           |                         |           |                       | 185 7               |
| Total <sup>10</sup>                        | 106       | 72,222                  | 120,000 7   | 59.9 <sup>7</sup>     | 6,400 7             | 103       | 74,689                  | 120,000 7 | 62.2 7                | 6,170 7             |
| Puerto Rico                                | 2         | 783                     | 1,780       | 44.0                  | 29 7                | 2         | 610                     | 1,780     | 34.2                  | 54 7                |
| Grand total <sup>10</sup>                  | 108       | 73,005                  | 122,000 r,7 | 59.7 7                | 6,430 7             | 105       | 75,298                  | 122,000 7 | 61.8 7                | 6,230 7             |

(Thousand metric tons unless otherwise specified)

Revised. -- Zero.

<sup>1</sup>Even where presented unrounded, data are thought to be accurate to no more than three significant digits. Includes data for white cement. Includes cement made from imported clinker.

<sup>2</sup>District assignation is the location of the reporting facilities. Specific districts include importers where district assignations were possible.

<sup>3</sup>Data include a small amount of portland cement subsequently consumed at the plant to make masonry cement; the amount thus double-counted cannot be determined precisely because of the involvement of cement stockpiles, but is less than 0.5% of the grand totals listed.

<sup>4</sup>Based on fineness needed to produce a plant's normal output mix, including masonry cement, and allowing for downtime for routine maintenance.

<sup>5</sup>Calculated relative to portland cement output; utilization would be higher if calculated to include output of masonry cement.

<sup>6</sup>Includes imported cement and stocks of domestic and imported cement at mills, and terminals, and in transit.

<sup>7</sup>Includes estimates for nonrespondents or facilities that provided incomplete information.

<sup>8</sup>Adjusted to avoid double-counting of portland cement supplied by one plant to another for the sole purpose of conversion to blended or masonry cement.

<sup>9</sup>Includes only those importers or terminals for which district assignations were not possible.

<sup>10</sup>May not add to totals shown because of independent rounding.

#### **Market Demand**

As cement production increases, the demand for pozzolans and SCMs increases. The volume of pozzolans and SCMs used for the production of cement remains relatively small compared to the total volume of cement produced. Current data is not yet available, but Table 13 shows the relative proportion in 2013.

For decades, both class C and class F fly ash met the majority of the market demand for pozzolanic materials, but, beginning in about 2010, concern for green house gas and trace element emissions prompted changes in the regulatory framework for a number of industries. Specifically, industries have to reduce CO<sub>2</sub> emissions and emission of trace elements like mercury. At about the same time, the price of natural gas dropped, making it more cost effective for a number of coal fired power plants to switch from coal to natural gas. As a result, a number of power plants switched to natural gas attendant with the reduction of fly ash as a waste product.

The allowable trace element concentrations also have been reduced, forcing coal power plants to scrub the ash with activated carbon, which can result in altering the fly ash such that it fails to meet the LOI requirements of ASTM C618. Although the volume of fly ash used has remained the same or increased since 2010, the supply has begun to dwindle, and a shortage of fly ash is on the horizon (Caltrans, 2016, p. 3 and 6). More coal-fired power plants are scheduled to switch to alternative fuel in the next few years. This shortened supply of fly ash eventually will increase its cost or the cost of any fly ash substitute, e.g., NP. The decline in volume and quality of fly ash is driving the growth in the NP market (b) (4)

Thus, cement producers are increasingly turning to broader use of pozzolans and SCMs to extend and enhance cement. As the cement and concrete industry become more accustomed to use of NP and are educated about the options available to tailor various types of cements to specific applications, the use of NP will undoubtedly increase (b) (2)



The reported total volume of NP produced in 2013 was only about 52,000 metric tons Table (b) (4)

# Table 13. Proportion of raw materials used in the production of portland cement. Table adoptedfrom von Oss (2015, p. 16.13).RAW MATERIALS USED TO PRODUCE CLINKER AND CEMENT IN THE UNITED STATES<sup>1,2</sup>

|   | 20      | 12                  | 2013    |                     |  |
|---|---------|---------------------|---------|---------------------|--|
| Material  | Clinker | Cement <sup>3</sup> | Clinker | Cement <sup>3</sup> |  |
| Calcareous:   |         |                     |         |                     |  |
| Limestone (aragonite, chalk, coral, marble)               | 86,800  | 1,720               | 90,530  | 1,930               |  |
| Cement rock (includes marl)                               | 8,310   | 12                  | 9,410   | 23                  |  |
| Cement kiln dust (CKD) <sup>4</sup>                       | 10      | 137                 | 50      | 136                 |  |
| Lime <sup>4</sup>   | 40      | 53                  | 73      | 38                  |  |
| Other   | 80      | 9                   | 75      | 4                   |  |
| Aluminous:  |         |                     |         |                     |  |
| Clay  | 3,310   |                     | 3,260   |                     |  |
| Shale and schist  | 2,330   | 50                  | 2,130   | 39                  |  |
| Other <sup>5</sup>  | 418     |                     | 545     |                     |  |
| Ferrous:  |         |                     |         |                     |  |
| Iron ore  | 608     |                     | 671     |                     |  |
| Mill scale  | 713     |                     | 656     |                     |  |
| Other <sup>6</sup>  | 25      |                     | 84      |                     |  |
| Siliceous:  |         |                     |         |                     |  |
| Sand, calcium silicates                                   | 3,170   |                     | 3,100   |                     |  |
| Sandstone, quartzite, soils, nonpozzolanic rocks          | 563     |                     | 738     |                     |  |
| Fly ash   | 2,410   | 137                 | 2,580   | 135                 |  |
| Other ash, including bottom ash                           | 1,230   |                     | 1,050   |                     |  |
| Granulated blast furnace slag <sup>7</sup>                | 8       | 224                 |         | 237                 |  |
| Other blast furnace slag                                  | 85      |                     | 35      |                     |  |
| Steel slag  | 444     |                     | 390     |                     |  |
| Other slag  | 84      |                     | 199     |                     |  |
| Natural rock pozzolans <sup>8</sup>                       |         | 40                  |         | 52                  |  |
| Other pozzolans <sup>9</sup>                              | 5       | 2                   | 1       | 3                   |  |
| Other:  |         |                     |         |                     |  |
| Gypsum and anhydrite                                      | (10)    | 3,920               | (10)    | 4,020               |  |
| Miscellaneous <sup>11</sup>                               | 76      | 39                  | 38      | 27                  |  |
| Total <sup>12</sup>                                       | 111,000 | 6,340               | 116,000 | 6,640               |  |
| Clinker, imported, raw materials equivalent <sup>13</sup> |         | 1,390               |         | 1,260               |  |
| Grand total <sup>12</sup>                                 | 111,000 | 7,730               | 116,000 | 7.890               |  |

(Thousand metric tons)

-- Zero.

<sup>1</sup>Excludes Puerto Rico.

<sup>2</sup>Data have been rounded to no more than three significant digits.

<sup>3</sup>Includes portland, blended, and masonry cements.

<sup>4</sup>Data are probably underreported.

<sup>5</sup>Includes alumina, aluminum dross, bauxite, spent catalysts, and other aluminous materials.

<sup>6</sup>Includes iron sludges, pyrite, and other ferrous materials.

<sup>7</sup>Includes both ground and unground material.

<sup>8</sup>Includes pozzolana and burned clays or shales (except where directly reported as clay or shale).

<sup>9</sup>Includes diatomite, silica fume, other microcrystalline silica, and other pozzolans, even if not used as such.

<sup>10</sup>Included with Calcareous: Other.

<sup>11</sup>Includes fluorspar and all other materials not listed earlier.

<sup>12</sup>May not add to totals shown because of independent rounding.

<sup>13</sup>Converted as 1.7 times the weight of foreign clinker consumed.

61

## (b) (4) ;(b) (4)

The overwhelming factor that is driving the demand for natural pozzolan is the reduced supply of fly ash and other pozzolanic materials and particularly class F fly ash in the western U.S. (0)(4). The fly ash supply is dwindling because of coal-fired power plant changes, the GGBFS supply is dwindling because the steel industry is relying more on overseas iron production, and silica fume supply continues to be tenuous because so few companies produce silica fume. Also, the cement industry is under pressure from governments to reduce CO<sub>2</sub> emissions through cement extenders (The cement industry accounts for approximately 5% of the global CO<sub>2</sub> emissions; Wikipedia, (b) (4)

## Market Entry

A number of deposits have attempted to produce NP in the last several decades; however, only three have been able to produce products and maintain a place in the NP market. Simply, the market for pozzolan and SCMs has been dominated by fly ash and GGBFS because of available supply, and very low volume, special application very high strength concrete needs have been met with silica fume. Using by-products as extenders and enhancers reduces the need for portland cement and uses a product created from expending energy to create another product or electricity. If by-products are not used, they have to be disposed at extra cost, so companies have great incentive to market their waste to reduce the overall cost of operations. This practice is cost effective for the manufacturers and energy producers. Companies that produce iron or electricity typically contract with a mineral admixture marketer or slag processor to handle their by-products and deliver it to cement companies for processing (Hoffman, 2006, p. 1164).



Market entry can only be achieved if the NP product can meet all and far exceed some of the ASTM C618 requirements. Higher end natural pozzolans sell for high enough price to compete with fly ash, but those that barely make C 618 do not sell for a high enough price. If the deposit product can vastly exceed C 618 standards, then it will make it. Right now, the western states are sold out of natural pozzolans because of the fly ash shortage, so any deposit that can meet buyer

specifications and exceed the standard has a very good chance of market entry (b) (4)



and compete very well in the growing NP market in the western and southwestern U.S. It may well compete in the international market if the product meets special niche application requirements.











#### **Common Variety vs Uncommon Variety Opinion**

The use of pozzolans and supplementary cementitious materials has become a critical component of the cement and concrete industries. Pozzolans are used by cement and concrete producers to extend and enhance ordinary portland cement, so much that pozzolans now are used to tailor the products to specific applications and sales contracts. Rather than vary the raw meal in cement manufacture and change the conditions of kiln, a costly endeavor, cement producers can tailor their product by using available pozzolans to manufacture many kinds of cement.

Artificial pozzolan supply is dwindling (particularly class F fly ash), but also ground granulated blast furnace slag because iron and steel manufacture is dwindling in the U.S. Cement and concrete producers naturally are turning once again to natural pozzolans to meet demand, and they are willing to pay premium prices for them. Most likely, buyers will continue to pay a premium price given the current political climate to reduce green house gases and move from coal to cleaner fuel sources. Both class F and class C fly ash supply will eventually be exhausted, paving the way for the return of the market for natural pozzolans with various characteristics.

Pozzolans are now as much a part of cement manufacture as materials that make up the raw meal themselves. Natural pozzolans now are similar and as critical in the manufacture of cement and concrete as high purity limestones that were given uncommon variety status by the legislative history of the Common Varieties Act (30 U.S.C. §§ 611-615) and the BLM regulations at 43 CFR 3830.12, materials once thought to be uncommon varieties simply because they were used in the manufacture of cement. The value of natural pozzolans is recognized in the increasing price they command in the market, significantly higher than a typical common variety aggregate used only as an extender or similar deposit used to manufacture block. Natural pozzolans are both an extender and an enhancer for the cement and concrete industries, and producers are willing to pay commensurate prices for natural pozzolans that do not require extensive drying, calcination, or additional processing clearly are valued higher than those deposits that do. However, even deposits that require additional processing are bringing premium prices in the market because they can be used to meet very specific and critical concrete design needs.

The intrinsic amorphous physical character of the Kirkland tuff, its chemical composition, and its apparent reactive performance allows it to fall within the elite of natural pozzolan deposits, deposits that have a distinct and special value because of their characteristics beyond the value of a typical common variety material. It is an uncommon variety deposit because it is critical in

cement manufacture given the economics of industry, because the material will bring a price in the market at least twice and up to several times the value of a common variety material in a similar market. The value differential between the cost of production and price is significantly higher than a typical common variety material. The intrinsic characteristics that will allow it to be sold without extensive drying or costly calcination makes it unique even among many of the other natural pozzolan deposits.

The value of the pumice in northern AZ from the White Vulcan claims allowed a pumice deposit to be determined an uncommon variety when the laundry market for stone wash jeans was expanding (cf. U.S. v.Multiple Use, Inc. (120 IBLA 063; 1991)). Buyers were willing to pay a premium price for the product. A similar situation occurred in New Mexico with the Copar Pumice Co., Inc., pumice mine (cf. Copar Pumice Co., Inc., v. Tidwell, 603 F.3d 780 (10th Cir.2010). When that market waned, the value of the deposit was reduced, and the same deposit once determined to be an uncommon variety deposit became a common variety deposit. In this case, the market for natural pozzolan and its value expanded in the mid 20th century when large pour dams were being built in the western U.S., but the market was overtaken with the use of an artificial pozzolan fly ash, essentially a waste product substitute with no home until its use in the cement and concrete industries. With the current move toward cleaner operations, less carbon dioxide, and less deleterious trace elements, fly ash supply and quality is dwindling. The demand for and value of natural pozzolans is again rising and likely to continue to rise. Deposits like the Kirkland tuff is perfectly suited to meet the demand, and buyers are willing to pay a premium price for the commodity. It is essentially a Copar pumice case in reverse. The quality of the deposit most likely will allow it to compete and be highly valued in niche cement markets, too.



In my opinion, the Kirkland tuff on the Capital association placer mining claim has intrinsic characteristics that will give it a distinct and special value in the market place. It is an uncommon variety deposit.

#### Conclusions

The Kirkland tuff on the Capital association placer mining claim is unique in that its physical and chemical characteristics will allow it to be used for a number of industrial applications. It has been extensively tested through drilling and sampling, and data from that testing combined with field observations and market research indicate the deposit can be used as a natural pozzolan and compete efficiently in the growing natural pozzolan market.



Changing technology in concrete design, more stringent application specifications, and dwindling supply of other pozzolanic materials have created a market for natural pozzolan in which cement manufacturers and concrete companies are looking and paying for versatile materials to lower their costs and still meet very rigid contract specifications. Those buyers are willing to pay a premium price well above a price typically paid for a common variety materials for consistent product performance. The Kirkland tuff on the Capital placer mining claim can compete and excel in this new viable market place.

Thus, it's intrinsic chemical and physical characteristics impart to it a distinct and special value in the market place, a value at least twice the value of similar common variety materials. Also, its characteristics will allow it to be mined and processed at less cost than many other deposits of natural pozzolan because it does not need to be extensively dried nor calcined. It has a value even greater than competing deposits of natural pozzolan. Thus, in my opinion, the Kirkland tuff on the Capital association placer mining claim MC is an uncommon variety deposit.

#### Recommendations

I recommend that BLM use this report and data as a supplement to the common variety determination required by 43 CFR subpart 3809.101 (a). In my opinion, the BLM should consider and treat the Kirkland tuff on the Capital association placer mining claim as an uncommon variety deposit under the General Mining Law and apply the 43 CFR subpart 3809 regulations for permitting actions instead of the 43 CFR subpart 3600 regulations that guide mineral material development.

During this investigation, I found ample data to suggest that a number of high value products potentially can be produced from this deposit. Therefore, I also recommend that, as analytical and market data becomes available for other applications, further investigations be conducted for the Kirkland tuff as supplements to this report and the BLM common variety determination to determine whether the deposit will meet the McClarty standards as an uncommon variety deposit

for those other commodities. This deposit may well contain several commodities that can be produced to the benefit of society and the public.

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### Appendices

**Appendix A - Land Status Maps** 

Master Title Plats Portions of Township 13 North, Range 4 West, Gila and Salt River Meridian, Arizona



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|------------|------|---------|
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### TOWNSHIP 13 NORTH RANGE 4 WEST OF THE GILA AND SALT RIVER MERIDIAN, ARIZONA

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Portion of the 1984 U.S. Bureau of Land Management (BLM) Surface and Mineral Estate Status Map, Bradshaw Mountains Quadrangle, showing land status of the lands surrounding the subject site. Secs. 28 and 33, T. 13 N., R. 4 W., G&SRM, are shown in the center of the map. White indicates private, blue indicates state, and yellow indicates federal (BLM) surface. Overlain vertical lines indicate subsurface estate administered by the BLM.

**Appendix B - Mining Claim Reports** 

#### UNITED STATES DEPARTMENT OF THE INTERIOR BUREAU OF LAND MANAGEMENT MINING CLAIM GEOGRAPHIC REPORT LIST OF MINING CLAIMS BY SECTION

Serial Num Mer Twn Rng Sec Quad Lead File Loc Dt Last Assmt Claim Name/Number Claimant(s) Casetype Status AMC367119 CAPITAL AMC367119 PLACER ACTIVE 07/15/2005 14 0130N 0040W 028 SW ZOUVAS ANNE 2017 AMC367119 14 0130N 0040W 028 SW CAPITAL ZOUVAS ARETA AMC367119 PLACER ACTIVE 07/15/2005 2017 AMC367119 14 0130N 0040W 028 SW CAPITAL ZOUVAS LUKE C AMC367119 PLACER ACTIVE 07/15/2005 2017 AMC367119 14 0130N 0040W 028 SW CAPITAL ZOUVAS MARIA AMC367119 PLACER ACTIVE 07/15/2005 2017 AMC367119 14 0130N 0040W 028 SW CAPITAL ZOUVAS MARK AMC367119 PLACER ACTIVE 07/15/2005 2017 AMC367119 CAPITAL AMC367119 07/15/2005 14 0130N 0040W 028 SW ZOUVAS MATTHEW PLACER ACTIVE 2017 AMC367119 14 0130N 0040W 028 SW CAPITAL ZOUVAS PETER A AMC367119 PLACER ACTIVE 07/15/2005 2017 AMC367119 14 0130N 0040W 028 SW CAPITAL ZOUVAS PETER S AMC367119 PLACER ACTIVE 07/15/2005 2017 AMC428988 14 0130N 0040W 028 SW,SE CAPITAL ONE KIRKLAND MINING CO AMC428988 LODE ACTIVE 06/11/2014 2017 AMC428989 14 0130N 0040W 028 SW.SE CAPITAL TWO KIRKLAND MINING CO AMC428988 LODE ACTIVE 06/11/2014 2017 AMC428990 14 0130N 0040W 028 SW.SE CAPITAL THREE KIRKLAND MINING CO AMC428988 LODE ACTIVE 06/11/2014 2017 KIRKLAND MINING CO AMC428991 CAPITAL FOUR AMC428988 LODE 06/11/2014 2017 14 0130N 0040W 028 SW,SE ACTIVE AMC428992 14 0130N 0040W 028 SW CAPITAL FIVE KIRKLAND MINING CO AMC428988 LODE ACTIVE 06/11/2014 2017 AMC428993 14 0130N 0040W 028 SW CAPITAL SIX KIRKLAND MINING CO AMC428988 LODE ACTIVE 06/11/2014 2017 AMC428994 LODE 14 0130N 0040W 028 SW CAPITAL SEVEN KIRKLAND MINING CO AMC428988 ACTIVE 06/11/2014 2017 AMC428995 14 0130N 0040W 028 SW CAPITAL EIGHT KIRKLAND MINING CO AMC428988 LODE 06/11/2014 ACTIVE 2017 Serial Num Claim Name/Number Lead File Status Loc Dt Last Assmt Mer Twn Rng Sec Ouad Claimant(s) Casetype PLACER AMC371346 14 0130N 0040W 033 NW HOMESTEAK ZOUVAS ANNE AMC371346 ACTIVE 04/02/2006 2 0 1 7 AMC371346 14 0130N 0040W 033 NW HOMESTEAK ZOUVAS ARETA AMC371346 PLACER ACTIVE 04/02/2006 2017 AMC371346 14 0130N 0040W 033 NW HOMESTEAK ZOUVAS LUKE C AMC371346 PLACER ACTIVE 04/02/2006 2017 AMC371346 14 0130N 0040W 033 NW HOMESTEAK ZOUVAS MARIA AMC371346 PLACER ACTIVE 04/02/2006 2 0 1 7 AMC371346 04/02/2006 AMC371346 14 0130N 0040W 033 NW HOMESTEAK ZOUVAS MARK PLACER ACTIVE 2017 AMC371346 14 0130N 0040W 033 NW HOMESTEAK ZOUVAS MATTHEW AMC371346 PLACER ACTIVE 04/02/2006 2017 AMC371346 PLACER 04/02/2006 AMC371346 14 0130N 0040W 033 NW HOMESTEAK ZOUVAS PETER A ACTIVE 2017 AMC371346 04/02/2006 AMC371346 14 0130N 0040W 033 NW HOMESTEAK ZOUVAS PETER S PLACER ACTIVE 2017 AMC432946 14 0130N 0040W 033 NW HOMESTEAK #1 KIRKLAND MINING CO AMC432946 LODE ACTIVE 03/11/2015 2017 AMC432946 LODE AMC432947 14 0130N 0040W 033 NW HOMESTEAK #2 KIRKLAND MINING CO ACTIVE 03/11/2015 2017 KIRKLAND MINING CO AMC432946 LODE 03/11/2015 2017 AMC432948 14 0130N 0040W 033 NW HOMESTEAK #3 ACTIVE AMC432949 14 0130N 0040W 033 NW HOMESTEAK #4 KIRKLAND MINING CO AMC432946 LODE ACTIVE 03/11/2015 2017 KIRKLAND MINING CO AMC432946 03/11/2015 AMC432950 14 0130N 0040W 033 NW HOMESTEAK #5 LODE ACTIVE 2017 AMC432951 14 0130N 0040W 033 NW HOMESTEAK #6 KIRKLAND MINING CO AMC432946 LODE ACTIVE 03/11/2015 2017 AMC432952 14 0130N 0040W 033 NW HOMESTEAK #7 KIRKLAND MINING CO AMC432946 LODE ACTIVE 03/11/2015 2017 AMC432953 14 0130N 0040W 033 NW HOMESTEAK #8 KIRKLAND MINING CO AMC432946 LODE ACTIVE 03/11/2015 2017

NO WARRANTY IS MADE BY BLM FOR THE USE OF THE DATA FOR PURPOSES NOT INTENDED BY BLM

Appendix C - Tabulated Sample Summary



**Appendix D - Photo Documentation of Samples** 






































Appendix E - Chain Of Custody Documents

























Appendix F - Mineralogy and Chemical Analyses




























































































Appendix G - Chemical and Physical Test Data - Natural Pozzolans






















Appendix H - Other Deposit Data
















































Figures



Fig. 1. Location map of the Kirkland tuff deposit, Yavapai County, Arizona. Map modified from Ninyo & Moore (2015, Fig. 1, p. 8).



Fig. 2. Topographic and mining claim location map, Kirkland tuff deposit, Yavapai County, Arizona. Map modified after the U.S. Geological Survey, Kirkland, Arizona, 7.5' topographic quadrangle map (2014). Universal transverse mercator coordinates (UTM) shown with yellow lines, zone 12, 1983 North American Datum.



Fig. 3. Air photo showing the Capital association placer mining claim (modified from Google Earth ,January 4, 2017).



Fig. 4. Terrain and strata along the western side of the Capital MC.

Photo taken from UTM coordinates 344664 mE., 3811656 mN., zone 12, NAD 83, looking due north along the western boundary of the Capital MC. Tuff beds strike approximately N. 40° W. and dip approximately 15-20° to the NE. The tuff is variably indurated due to silica content which results in differential erosion. Tuff beds in the left and middle ground of the photo are more indurated than the beds immediately underlying the basalt cap in the photo background. Cliffs in the indurated tuff in the right middle ground of the photo are approximately 50 feet high for scale. Photo by C. Wilson, June 26, 2016.



Fig. 5. Terrain and quarry in the west central Capital MC.

Photo of the historical quarry on the Capital MC taken from UTM 344664 mE., 3811656 mN., zone 12, NAD 83 looking N. 45° E.. Aerial view of the quarry is shown in Fig. 3. The access road to the site approaches from the left of the photo and is visible in the central foreground. Dark ridge in the photo middle ground is a basalt that overlies the lithic tuff. Cliffs at far right middle ground are 75-100 feet high for scale. Photo by C. Wilson, June 26, 2016.



Fig. 6. Terrain and stockpile in west central part of the Capital MC.

Photo looking due east across the west central part of the Capital MC from UTM coordinates 344664 mE., 3811656 mN., zone 12, NAD 83. Cliff in the photo middle ground is indurated tuff, and light colored tuff stockpile is shown in the middle ground at the right in the photo. Cliff in the middle ground is approximately 150 feet high for scale. Photo by C. Wilson, June 26, 2016.



Fig. 7. Terrain and stockpile in the western and southwestern part of the Capital MC.

Photo of stratified tuff and overlying stockpile in the western part of the Capital MC. Light colored stockpile in the left middle ground of the photo was extracted from the quarry shown in Fig. 5. Photo looking S. 70° E. from UTM coordinates 344664 mE., 3811656 mN., zone 12, NAD 83. Bushes on top of the stockpile are approximately seven feet high for scale. Photo by C. Wilson, June 26, 2016.



Fig. 8. Terrain across the quarry in the west central part of the Capital MC.

Photo looking N. 85° W. across the historic quarry in the west central Capital MC from UTM coordinates 344978 mE., 3811791 mN, zone 12, NAD 83. Stockpile shown in Figs. 6 and 7 is just behind and to the left of this photo site. Quarry wall in left middle ground of photo is approximately 75 feet high; quarry wall in right middle ground is approximately 40 feet high. Photo by C. Wilson, June 26, 2016.



Fig. 9. Terrain and strata in the central and north central parts of the Capital MC.

Photo looking N. 45° W. across the central and north central parts of the Capital MC from UTM coordinates 344978 mE., 3811791 mN., zone 12, NAD 83. The eastern boundary of the quarry shown in Fig. 5 is in the far left middle ground of the photo, and the quarry wall is approximately 40 feet high for scale. Basalt forms the darker colored ridge in the right middle ground of the photo. It immediately overlies the lithic tuff and is approximately 20 feet thick at this site. Photo by C. Wilson, June 26, 2016.



Fig. 10. Eastern claim line of the Capital Six lode mining claim in the central part of the Capital MC.

Lithic tuff is exposed in the foreground of the photo, and basalt forms the ridgeline in the photo background. A white polyvinyl chloride (PVC) post at the southeast corner of the Capital Six lode mining claim is visible behind the bush in central foreground of the photo. The white post on the hillside of the ridge in the background is the east end center post of the Capital Six. View is looking N. 9° W. along the eastern boundary of the Capital Six in the central Capital MC from UTM coordinates 344977 mE., 3811790 mN., zone 12, NAD 83. Photo by C. Wilson, June 26, 2016.



Fig. 11. Historic stockpile in the western part of the Capital MC.

Stockpile from historic mining in the western part of the Capital MC. Photo taken from UTM coordinate 344998 mE., 3811652 mN., zone 12, NAD 83. Looking S. 65° W. a portion of the stock pile is planning on being mined. The left side of the stock pile in the photo is approximately 50 feet high from toe to crest. Photo by C. Wilson, June 26, 2016.



Fig. 12. Terrain in the south central part of the Capital MC.

Photo showing outcrops of indurated tuff in the south central part of the Capital MC. Stockpile in the photo middle ground is approximately 50 feet high for scale. Photo taken from near the southern boundary of the Capital MC at UTM coordinate 345019 nE., 3811387 mN., zone 12, NAD 83, looking N. 35° W. Photo by C. Wilson, June 26, 2016.



Fig. 13. Outcrops and terrain in the southeastern part of the Capital MC.

Photo shows outcrops of indurated tuff and terrain in the southeastern part of the Capital MC. Outcrop cliff is approximately 75 feet high for scale. The southeast corner of the Capital MC approximately lies about 20 feet below the ridge crest at the first break in slope on the far ridge line in the right photo background. Photo taken from UTM coordinate 345153 mE., 3811637 mN., zone 12, NAD 83, looking S. 25° E. Photo by C. Wilson, June 26, 2016.



Fig. 14. Outcrops and terrain in the southeastern part of the Capital MC.

Photo looking S. 44° W. from UTM coordinate 345707 mE., 3811364 mN., zone 12, NAD 83, across the southeastern corner of the Capital MC. All rocks in the photo middle ground are bedded tuffs dipping to the northeast from five to 15°. Outcrops are about 50 feet high for scale. The southeast corner of the Capital MC Photo is approximately on the outcrops in the left center photo about 1,000 feet distant. The row of cottonwood trees along the wash in the photo background is approximately the boundary between the Capital MC and the Homesteak MC. Photo by C. Wilson, June 26, 2016.



Fig. 15. Outcrops and terrain in the eastern part of the Capital MC.

Photo looking approximately N. 50° W. from UTM coordinate 345707 mE., 3811364 mN., zone 12, NAD 83, across the east central part of the Capital MC. Bush on the top of the outcrop in the right central part of the photo is about 10 feet tall for scale. The eastern boundary of the Capital MC is approximately where the outcrops begin in the photo. The light colored stockpile in the west central part of the Capital MC is the central middle ground of the photo right over the top of the closer outcrops and before the far ridge in the background. The historic quarry is in the right middle ground of the photo. Photo by C. Wilson, June 26, 2016.



Fig. 16. Physiographic map of Arizona showing the Kirkland tuff deposit location. Map shows major physiographic subdivisions in Arizona. Physiographic provinces are in bold lettering, subprovinces in intermediate lettering, and sections are in small lettering. Subdivisions are based on variations in generalized topography. Map modified after Menges and Pearthree (1989, p. 651).





Map symbols: Xb, Xgc, Ykp - Precambrian basalt, tonalite, and alkali granite; Tso-Miocene sedimentary and volcaniclastic rocks; Tbo, Tto-Pliocene basalt and tuff; QTs-Pleistocene and Pliocene sedimentary and volcaniclastic rocks; Qal-Holocene alluvium. Map modified after DeWitt, et al. (2008).







Map modified from U.S. Geological Survey (2016). Subject site is about 15 miles southwest of Prescott, Arizona.



(b) (4)

| Unit | Description   | Thickness |
|------|---|-----------|
| 1    | Basalt agglomerate  | unknown   |
| 2    | Conglomerate, subangular pebble to cobble sized granite and schist, and some cinder   |           |
|      | fragments . Soft and crumbly .  | 60 ft.    |
| 3    | Basalt, massive with weathered olivine<br>crystals. Agglomeratic at top where it<br>grades into a tuff.   | 15 ft.    |
| 4    | Whitish tuff, base of tuff composed mostly of<br>cobble to boulder sized pieces of basalt<br>grading upward into pebble sized granitic<br>and schistic subangular material in a whitish<br>tuff (ash?) matrix. This zone is approximately<br>60% tuff, 40% rock fragments. Medium hardness. | 30 ft.    |
| 5    | Tan tuff, hard vitric glass chards containing<br>about 40 to 60% rock fragments of basalt,<br>granite, and schist.  | 30 ft .   |
| 6    | Whitish tuff, same description as unit 4.   | 40 ft.    |
| 7    | Tan tuff, same description as unit 5.   | 80 ft.    |
| 8    | Whitish tuff, same description as unit 4.   | 50 ft.    |
| 9    | Basalt, dark gray with some fracturing.   | 20-60 ft. |

Fig. 20. Type section of interbedded volcanic and volcaniclastic rocks in Sec. 33, T. 13 N., R. 4 W., G&SRM.

Stratigraphic section from Randall (1974, p. 13).



Fig. 21. Indurated zone in the upper lithic tuff bed on the Capital MC.

Photo of a low rounded outcrop in the upper tuff bed on the Capital MC. This bleached zone is a matrix supported lithic tuff with angular to subangular clasts of individual minerals mafic volcanic rocks, granites, and metamorphic rocks from 0.5 mm to 4.0 cm in diameter in a silicified, pumiceous matrix. The silicification either from devirtrification or hydrothermal alteration results in induration of the tuff and differential erosion. Photo taken from UTM coordinates 345062 mE., 3811696 mN., zone 12, NAD 83, looking S. 85° W. Photo by C. Wilson, June 26, 2016.



Fig. 22. Flow diagram for the manufacture of cement.

Diagram adopted from van Oss (2005, p. 20). Note that pozzolans typically are added to the clinker at the kiln tailgate for the production of blended cements. They also may be added to the finished cement product by a customer or construction company at the same time as aggregates during the production of concrete.



## SAND & GRAVEL

| A.B.C              | 27.99 TN |
|--------------------|----------|
| Arena Sand         | 30.99 TN |
| Concrete Sand      | 30.99 TN |
| Concrete Mix       | 30.99 TN |
| Grout Mix          | 30.99 TN |
| Washed Mortar Sand | 30.99 TN |
| USGA Sand          | 49.99 TN |

## **RIVER ROCK**

| 3/8" Pea Gravel          | 33.99 TN |
|--------------------------|----------|
| 1/2" - 1" River Rock     | 33.99 TN |
| 3/4" - 1 1/2" River Rock | 33.99 TN |
| 1-1/2" - 3" River Rock   | 33.99 TN |
| 3" - 6" River Rock       | 34.99 TN |
| 6"+ Cobble               | 34.99 TN |

## MEXICAN BEACH PEBBLES

| 50 Lb. Bag - Polished   | 35.99 Bag |
|-------------------------|-----------|
| 75 Lb. Bag - Unpolished | 30.99 Bag |

## **SOILS & SOIL MIXTURES**

| Fill Dirt           | 16.99 TN      |
|---------------------|---------------|
|                     |               |
| DECORATIVE ROCK     |               |
| Madison Gold        | A CONTRACT OF |
| 1/4" Minus          | 31.99 TN      |
| 1/4" Screened       | 33.99 TN      |
| 1/2" Minus          | 46.99 TN      |
| 3/4" Screened       | 46.99 TN      |
| 1/2" Screened       | 53.99 TN      |
| 3/4" Sized          | 53.99 TN      |
| Palomino Gold       |               |
| 1/2"or 1" Screened  | 54.99 TN      |
| Pink Coral          |               |
| 1/2" or 1" Screened | 54.99 TN      |
| Red Cinder          |               |
| 1" Screened         | 47.99 YD      |
| Saddleback Brown    |               |
| 1/2" or 1" Screened | 51.99 TN      |
| Sedona Red          |               |
| 1/2" & 1" Screened  | 53.99 TN      |
| Table Mesa Brown    |               |
| 3/8" Minus          | 41.99 TN      |
| 1/2" or 1" Screened | 59.99 TN      |
| Yavapai Coral       |               |
| 3/8" Minus          | 31.99 TN      |
| 3/8" Screened       | 42.99 TN      |
|                     |               |

Fig. 23. Example of common variety rock product prices, Phoenix, Arizona. Product brochure from Pioneer Landscaping Materials, Phoenix, Arizona, showing current retail prices for landscape gravel, crushed stone, and cinders. Obtained December 15, 2016.