





SAFETY DATA SHEET (SDS): LIMESTONE ROCK ASPHALT (LRA)

SECTION I – IDENTIFICATION

PRODUCT IDENTIFIER	TRADE NAME	OTHER SYNONYMS
Limestone Rock Asphalt (LRA)	Limestone Rock Asphalt (LRA)	None
RECOMMENDED USE AND RESTRICTION ON USE Used for construction purposes This product is not intended or designed for and should not be used as an abrasive blasting medium or for foundry applications.		
MANUFACTURER/SUPPLIER INFORMATION Martin Marietta Materials 2710 Wycliff Road Raleigh, North Carolina 27607 Phone: 919-781-4550 For additional health, safety or regulatory information and other emergency situations, call 919-781-4550		

SECTION II – HAZARD(S) IDENTIFICATION

HAZARD CLASSIFICATION: Category 1A Carcinogen Category 1 Specific Target Organ Toxicity (STOT) following repeated exposures Category 1 Eye Damage Category 2 Skin Irritant	 
SIGNAL WORD: DANGER	
HAZARD STATEMENTS: May cause cancer by inhalation. Causes damage to lungs, kidneys and autoimmune system through prolonged or repeated exposure by inhalation. Causes skin irritation and serious eye damage.	
PRECAUTIONARY STATEMENTS Do not handle until the safety information presented in this SDS has been read and understood. Do not breathe dusts or mists. Do not eat, drink or smoke while manually handling this product. Wash skin thoroughly after manually handling. If on skin: Rinse skin after manually handling and wash contaminated clothing if there is potential for direct skin contact before reuse. If swallowed: If gastrointestinal discomfort occurs and if person is conscious, give a large quantity of water and induce vomiting; however, never attempt to make an unconscious person drink or vomit. If inhaled excessively: Remove person to fresh air and keep comfortable for breathing. Administer oxygen and assist ventilation as required. If in eyes: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do, and continue rinsing. If exposed, concerned, unwell or irritation of the eyes, skin, mouth or throat/nasal passage persist: Get medical attention. Wear eye protection and respiratory protection following this SDS, NIOSH guidelines and other applicable regulations. Use protective gloves if manually handling the product. Avoid creating dust when handling, using or storing. Use with adequate ventilation to keep exposure below recommended exposure limits. Dispose of product in accordance with local, regional, national or international regulations. Please refer to Section XI for details of specific health effects of the components.	

SECTION III – COMPOSITION/INFORMATION ON INGREDIENTS

COMPONENT(S) CHEMICAL NAME	CAS REGISTRY NO	% by weight (approx)
Limestone	1317-65-3	80-99
Silicon Dioxide ⁽¹⁾ , SiO ₂	7631-86-9	0-10
Aluminum Oxide, Al ₂ O ₃	1344-28-1	<1
Ferric Oxide, Fe ₂ O ₃	1309-37-1	<1
Magnesium Oxide, MgO	1309-48-4	0-8
Calcium Oxide, CaO	1305-78-8	0-43
Sodium Oxide, Na ₂ O	1313-59-3	<1
Potassium Oxide, K ₂ O	12136-45-7	<1
Calcium Carbonate, CaCO ₃	1317-65-3	40-100
Asphalt Bitumen ⁽²⁾	8052-42-4	<1-20

(1): The composition of SiO₂ may be up to 100% crystalline silica

(2): CAS No. for Asphalt

SECTION IV – FIRST-AID MEASURES

INHALATION: If excessive inhalation occurs, remove to fresh air. Dust in throat and nasal passages should clear spontaneously. Administer oxygen and assist ventilation as required. Contact a physician if irritation or difficulty breathing persists or develops later.

EYES: Immediately flush eye(s) with plenty of clean water for at least 15 minutes, while holding the eyelid(s) open. Occasionally lift the eyelid(s) to ensure thorough rinsing. Remove contact lenses, if present and easy to do, and continue rinsing. Beyond flushing, do not attempt to remove material from the eye(s). Contact a physician if irritation, pain, swelling, lacrimation or photophobia persists or develops later.

SKIN: Rinse skin with soap and water after manually handling and wash contaminated clothing if there is potential for direct skin contact. Contact a physician if irritation persists or develops later.

INGESTION: If gastrointestinal discomfort occurs and if person is conscious, give a large quantity of water and induce vomiting; however, never attempt to make an unconscious person drink or vomit. Get medical attention.

SIGNS AND SYMPTOMS OF EXPOSURE: There are generally no signs or symptoms of exposure to respirable crystalline silica. Often, chronic silicosis has no symptoms. The symptoms of chronic silicosis, if present, are shortness of breath, wheezing, cough and sputum production. The symptoms of acute silicosis which can occur with exposures to very high concentrations of respirable crystalline silica over a very short time period, sometimes as short as 6 months, are the same as those associated with chronic silicosis; additionally, weight loss and fever may also occur. The symptoms of scleroderma, an autoimmune disease, include thickening and stiffness of the skin, particularly in the fingers, shortness of breath, difficulty swallowing and joint problems.

Direct skin and eye contact with dust may cause irritation by mechanical abrasion. Some components of the product are also known to cause corrosive effects to skin, eyes and mucous membranes. Ingestion of large amounts may cause gastrointestinal irritation and blockage. The petroleum distillates from the asphalt component may be absorbed from the gastrointestinal tract, with possible systemic effects (gastrointestinal irritation, vomiting, diarrhea, and CNS depression) and possible aspiration into the lungs. Aspiration of petroleum distillates has caused pulmonary edema and chemical pneumonitis. Inhalation of dust may irritate nose, throat, mucous membranes and respiratory tract by mechanical abrasion. Coughing, sneezing, chest pain, shortness of breath, inflammation of mucous membrane, and flu-like fever may occur following exposures in excess of appropriate exposure limits. Repeated excessive exposure may cause pneumoconiosis, such as silicosis and other respiratory effects.

SECTION V – FIRE-FIGHTING MEASURES**EXTINGUISHING AGENT**

Not flammable. For fires involving asphalt, dry chemical or carbon dioxide types of extinguishers are considered as most appropriate. Solid streams of water may be ineffective. Cool all affected containers with flooding quantities of water. Water or foam may cause frothing.

UNUSUAL FIRE AND EXPLOSION HAZARD

Contact with powerful oxidizing agents may cause fire and/or explosions (see Section X of this SDS). While individual components are known to react vigorously with water to produce heat, this is not expected from the LRA. When product is heated or comes in contact with sparks or flames, the vapors formed may result in explosive mixtures with air. Vapors may travel to source of ignition and flash back. May readily ignite when mixed with naphtha and other volatile solvents.

SPECIAL FIRE FIGHTING PROCEDURES

Since fire may produce toxic fumes, wear a self-contained breathing apparatus (SCBA) with a full face-piece operated in the pressure-demand or positive mode.

HAZARDOUS COMBUSTION PRODUCTS

Fires may produce irritating, corrosive and/or toxic gases. The health effects of these products are further discussed in Section XI.

SECTION VI – ACCIDENTAL RELEASE MEASURES**STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED**

Persons involved in cleaning should first follow the precautions defined in Section VII of the SDS.

If product is spilled, notify safety personnel, evacuate all unnecessary personnel, remove all heat and ignition sources and provide maximum explosion-proof ventilation. Cleanup personnel should protect against vapor inhalation and skin or eye contact. Use water spray to reduce vapors. For small spills, collect with sand or some noncombustible inert material and place in appropriate containers for disposal.

Spilled materials, where dust can be generated, may overexpose cleanup personnel to respirable crystalline silica-containing dust and other components that may pose inhalation hazards. Do not dry sweep spilled material. Collect the material using a method that does not produce dust such as a High-Efficiency Particulate Air (HEPA) vacuum or thoroughly wetting down the dust before cleaning up. Wear appropriate personal protective equipment as specified in Section VIII including appropriate respirators during and following clean up or whenever airborne dust is present to ensure worker exposures remain below occupational exposure limits (OELs - Refer to Section VIII).

Place the dust in a covered container appropriate for disposal. Dispose of the dust according to federal, state and local regulations.

This product is not subject to the reporting requirements of SARA Title III Section 313, and 40 CFR 372.

SECTION VII – HANDLING AND STORAGE

This product is not intended or designed for and should not be used as an abrasive blasting medium or for foundry applications. Follow protective controls set forth in Section VIII of this SDS when handling this product. Dust containing respirable crystalline silica and other components that may be corrosive/irritant may be generated during processing, handling and storage. Use good housekeeping procedures to prevent the accumulation of dust in the workplace.

Avoid inhalation of fumes if product is heated and contact with skin and eyes. Keep ignition sources away from vents and openings and do not breathe gases when opening hatches and dome covers. Do not store near heat, sparks, flame or strong oxidants.

Do not breathe dust. Avoid contact with skin and eyes. Do not store near food or beverages or smoking materials. Do not stand on piles of materials; it may be unstable.

Use adequate ventilation and dust collection equipment and ensure that the dust collection system is adequate to reduce airborne dust levels to below the appropriate OELs. If the airborne dust levels are above the appropriate OELs, use respiratory protection during the establishment of engineering controls. Refer to Section VIII - Exposure Controls/Personal Protection for further information.

SECTION VII – HANDLING AND STORAGE, CONTD.

In accordance with OSHA’s Hazard Communication Standard (29 CFR 1910.1200, 1915.99, 1917.28, 1918.90, 1926.59, 1928.21), state, and/or local right-to-know laws and regulations, familiarize your employees with this SDS and the information contained herein. Warn your employees, your customers and other third parties (in case of resale or distribution to others) of the potential health risks associated with the use of this product and train them in the appropriate use of personal protective equipment and engineering controls, which will reduce their risks of exposure.

See also ASTM International standard practice E 1132-06, "Standard Practice for Health Requirements Relating to Occupational Exposure to Respirable Crystalline Silica."

For safe handling and use of this product for Hydraulic Fracturing, please see the OSHA/NIOSH Hazard Alert Worker Exposure to Silica during Hydraulic Fracturing DHHS (NIOSH) Publication No. 2012-166 (2012).

http://www.osha.gov/dts/hazardalerts/hydraulic_frac_hazard_alert.pdf

SECTION VIII – EXPOSURE CONTROLS/PERSONAL PROTECTION

Airborne OELs for Components of LRA:

COMPONENT(S) CHEMICAL NAME	MSHA/OSHA PEL	ACGIH TLV-TWA	NIOSH REL
Limestone	(T) 15 mg/m ³ , (R) 5 mg/m ³	-	(T) 10 mg/m ³ , (R) 5 mg/m ³
Silicon Dioxide, SiO ₂	(R) 10 mg/m ³ / (% SiO ₂ + 2) §	(R) 0.025 mg/m ³ #	(R) 0.05 mg/m ³ #
Aluminum Oxide, Al ₂ O ₃	(T) 15 mg/m ³ , (R) 5 mg/m ³	(1) (R) 1 mg/m ³	-
Ferric Oxide, Fe ₂ O ₃	(2) 10 mg/m ³	(R) 5 mg/m ³	(3) 5 mg/m ³
Magnesium Oxide, MgO	(4) 15 mg/m ³	(I) 10 mg/m ³	-
Calcium Oxide, CaO	5 mg/m ³	2 mg/m ³	2 mg/m ³
Sodium Oxide, Na ₂ O (5)	2 mg/m ³	(C) 2 mg/m ³	(C) 2 mg/m ³
Potassium Oxide, K ₂ O	-	(6) (C) 2 mg/m ³	(6) (C) 2 mg/m ³
Calcium Carbonate, CaCO ₃	(T) 15 mg/m ³ , (R) 5 mg/m ³	-	(T) 10 mg/m ³ , (R) 5 mg/m ³
Asphalt Bitumen	-	(7)(I) 0.5 mg/m ³	-

§: Crystalline silica is normally measured as respirable dust. The OSHA/MSHA standard also presents a formula for calculation of the PEL based on total dust: 30 mg/m³ / (% SiO₂ + 2). The OSHA/MSHA PEL listed is for dust containing crystalline silica (quartz) and is based on the silica content of the respirable dust sample. The OSHA/MSHA PEL for crystalline silica as tridymite and cristobalite is one-half the PEL for crystalline silica (quartz).

The ACGIH and NIOSH limits are for crystalline silica (quartz), independent of the dust concentration. The ACGIH TLV for crystalline silica as cristobalite is equal to the TLV for crystalline silica as quartz. In 2005, ACGIH withdrew the TLV for crystalline silica as tridymite. Refer to Section X for thermal stability information for crystalline silica (quartz).

(1): Limits based on Aluminum Metal and Insoluble Compounds.

(2): As Iron Oxide Fume.

(3): Dust and fume, as Iron

(4): As Magnesium Oxide Fume Total Particulate.

(5): Based on Sodium Hydroxide.

(6): Based on Potassium Hydroxide.

(7): As Benzene-Soluble Aerosol

(R): Respirable Fraction.

(T): Total Dust.

(I): Inhalable Fraction.

(C): Ceiling Limit

Airborne OELs for Inert/Nuisance Dust:

Standard	Respirable Dust	Total Dust
MSHA/OSHA PEL (as Inert or Nuisance Dust)	5 mg/m ³	15 mg/m ³
ACGIH TLV (as Particles Not Otherwise Specified)	3 mg/m ³	*10 mg/m ³
NIOSH REL (Particulates Not Otherwise Regulated)	-	-

Note: The limits for Inert Dust are provided as guidelines. Nuisance dust is limited to particulates not known to cause systemic injury or illness.

* The TLV provided is for inhalable particles not otherwise specified.

SECTION VIII – EXPOSURE CONTROLS/PERSONAL PROTECTION, CONTD.**ENGINEERING CONTROLS**

Ventilation: Use local exhaust, general ventilation or natural ventilation adequate to maintain exposures below appropriate exposure limits.

Other control measures: Respirable dust and crystalline silica levels should be monitored regularly. Dust and crystalline silica levels in excess of appropriate exposure limits should be reduced by implementing feasible engineering controls, including (but not limited to) dust suppression (wetting), ventilation, process enclosure and enclosed employee work stations.

EYE/FACE PROTECTION

Safety glasses with side shields should be worn as minimum protection. Dust goggles should be worn when excessively (visible) dusty conditions are present or are anticipated. If irritation persists, get medical attention immediately. There is potential for severe eye irritation if exposed to excessive concentrations of dust for those using contact lenses.

SKIN PROTECTION

Use appropriate protective gloves if manually handling the product. If the material is heated, avoid direct contact with skin by using heat insulated gloves and protective clothing.

RESPIRATORY PROTECTION

Respirator Recommendations:

For respirable crystalline silica levels that exceed or are likely to exceed appropriate exposure limits, a NIOSH-approved particulate filter respirator must be worn. Respirator use must comply with applicable MSHA or OSHA standards, which include provisions for a user training program, respirator repair and cleaning, respirator fit testing, and other requirements. For additional information contact NIOSH at 1-800-356-4674 or visit website: <http://www.cdc.gov/niosh/npg> (search for crystalline silica). See also ANSI standard Z88.2 (latest revision) "American National Standard for Respiratory Protection," 29 CFR 1910.134 and 1926.103, and 42 CFR 84.

NIOSH recommendations for respiratory protection include:

Up to 0.5 mg/m³:

(APF = 10) Any particulate respirator equipped with an N95, R95, or P95 filter (including N95, R95, and P95 filtering facepieces) except quarter-mask respirators. The following filters may also be used: N99, R99, P99, N100, R100, P100.

Up to 1.25 mg/m³:

(APF = 25) Any powered, air-purifying respirator with a high-efficiency particulate (100-series) filter.

(APF = 25) Any supplied-air respirator operated in a continuous-flow mode

Up to 2.5 mg/m³:

(APF = 50) Any air-purifying, full-facepiece respirator with an N100, R100, or P100 filter.

(APF = 50) Any powered, air-purifying respirator with a tight-fitting facepiece and a high-efficiency particulate filter

Up to 25 mg/m³:

(APF = 1000) Any supplied-air respirator operated in a pressure-demand or other positive-pressure mode

If product is heated and fumes exceeding appropriate exposure limits are expected to be present, use any self-contained breathing apparatus that has a full face-piece and is operated in a pressure-demand or positive pressure mode or any supplied-air respirator that has a full face-piece and is operated in a pressure-demand or positive pressure mode in combination with an auxiliary self-contained positive-pressure breathing apparatus.

Supplied-air respirators must be used if the standard for hydrogen sulfide (H₂S) is exceeded or when entering confined or enclosed spaces where H₂S may be present.

Emergency or planned entry into unknown concentrations or IDLH conditions (50 mg/m³ for crystalline silica-quartz): A self-contained breathing apparatus (SCBA) that has a full-face piece and is operated in a pressure-demand or other positive-pressure mode or any supplied-air respirator that has a full-face piece and is operated in a pressure-demand or other positive-pressure mode in combination with an auxiliary self-contained positive-pressure breathing apparatus.

Escape from unknown or IDLH conditions: An air-purifying, full-face piece respirator with a high-efficiency particulate (100-series) filter or any appropriate escape-type, self-contained breathing apparatus.

SECTION VIII – EXPOSURE CONTROLS/PERSONAL PROTECTION, CONTD.**RESPIRATORY PROTECTION, CONTD.**

If the workplace airborne crystalline silica concentration is unknown for a given task, conduct air monitoring to determine the appropriate level of respiratory protection to be worn. Consult with a certified industrial hygienist, your insurance risk manager or the OSHA Consultative Services group for detailed information. Ensure appropriate respirators are worn, as needed, during and following the task, including clean up or whenever airborne dust is present, to ensure worker exposures remain below OELs.

GENERAL HYGIENE CONSIDERATIONS

There are no known hazards associated with this material when used as recommended. Following the guidelines in this SDS are recognized as good industrial hygiene practices. Avoid breathing dust. Avoid skin and eye contact. Wash dust-exposed skin with soap and water before eating, drinking, smoking and using toilet facilities. Wash work clothes after each use.

SECTION IX— PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE Gray particles ranging in size from powder to small stones.	ODOR AND ODOR THRESHOLD Mild petroleum odor; odor threshold - varied
pH AND VISCOSITY Not applicable	MELTING POINT/FREEZING POINT Not applicable
BOILING POINT AND RANGE Not applicable	FLASH POINT AND FLAMMABILITY* >450°F and not flammable
FLAMMABILITY/EXPLOSIVE LIMITS AND AUTOIGNITION TEMPERATURE* Not applicable and 905°F	EVAPORATION RATE AND DECOMPOSITION TEMPERATURE* <0.01 (ether=1) and not available
VAPOR PRESSURE AND VAPOR DENSITY IN AIR Not applicable	SPECIFIC GRAVITY. 2.188
SOLUBILITY IN WATER Negligible	PARTITION COEFFICIENT: N-OCTANOL/WATER Not applicable

SECTION X – STABILITY AND REACTIVITY

STABILITY Stable	CONDITIONS TO AVOID Avoid high temperatures, open flames, sparks, welding, smoking and other sources of ignition. Contact with incompatible materials (see below).
THERMAL STABILITY If crystalline silica (quartz) is heated to more than 870°C (1598°F), it can change to a form of crystalline silica known as tridymite, and if crystalline silica (quartz) is heated to more than 1470°C (2678°F), it can change to a form of crystalline silica known as cristobalite.	
INCOMPATIBILITY (Materials to avoid) Contact with powerful oxidizing agents such as fluorine, boron trifluoride, chlorine trifluoride, manganese trifluoride, and oxygen difluoride may cause fire and/or explosions. Some components of LRA may react vigorously with water. May readily ignite when mixed with naphtha and other volatile solvents.	
HAZARDOUS DECOMPOSITION PRODUCTS Silica dissolves in hydrofluoric acid producing a corrosive gas - silicon tetrafluoride. Thermal decomposition of the material may release carbon monoxide, carbon dioxide, hydrogen sulfide, nitrogen dioxide, ozone and other organic and inorganic compounds into the atmosphere due to the asphalt content. The health effects of the decomposition products are discussed in Section XI.	
HAZARDOUS POLYMERIZATION Not known to polymerize	

SECTION XI – TOXICOLOGICAL INFORMATION

Health Effects: The information below represents an overview of health effects caused by overexposure to one or more components in LRA.

Primary routes(s) of exposure: Inhalation Skin Ingestion

EYE CONTACT: Direct contact with dust may cause irritation by mechanical abrasion or corrosive action. Conjunctivitis may occur.

SKIN CONTACT: Direct contact may cause irritation by mechanical abrasion. Some components of material are also known to cause corrosive effects to skin and mucous membranes.

SKIN ABSORPTION: Not expected to be a significant route of exposure.

INGESTION: Small amounts (a tablespoonful) swallowed during normal handling operations are not likely to cause injury. Ingestion of large amounts may cause gastrointestinal irritation and blockage.

INHALATION: Dust may irritate nose, throat, mucous membranes and respiratory tract by mechanical abrasion. Coughing, sneezing, chest pain, shortness of breath, inflammation of mucous membrane, and flu-like fever may occur following exposures in excess of appropriate exposure limits.

MEDICAL CONDITIONS AGGRAVATED BY EXPOSURE

Inhaling respirable dust and/or crystalline silica may aggravate existing respiratory system disease(s) (e.g., bronchitis, emphysema, chronic obstructive pulmonary disease) and/or dysfunctions. Exposure to dust may aggravate existing skin and/or eye conditions. Smoking and obstructive/restrictive lung diseases may also exacerbate the effects of excessive exposure to this product.

This product is a mixture of components. The composition percentages are listed in Section III. Toxicological information for each component is listed below:

Silicon Dioxide: It is comprised of amorphous and crystalline forms of silica. In some batches, crystalline silica may represent up to 100% of silicon dioxide.

Exposure route: Eyes, respiratory system.

Target organs: Eyes, skin, respiratory system.

ACGIH, MSHA, and OSHA have determined that adverse effects are not likely to occur in the workplace provided exposure levels do not exceed the appropriate exposure limits. Lower exposure limits may be appropriate for some individuals including persons with pre-existing medical conditions as described under medical conditions aggravated by exposure.

A. SILICOSIS

The major concern is silicosis (lung disease), caused by the inhalation and retention of respirable crystalline silica dust. Silicosis leads to conditions such as lung fibrosis and reduced pulmonary function. The form and severity in which silicosis manifests itself, depends in part on the type and extent of exposure to silica dusts: chronic, accelerated and acute forms are recognized. In later stages the critical condition may become disabling and potentially fatal. Restrictive and/or obstructive changes in lung function may occur due to exposure. A risk associated with silicosis is development of pulmonary tuberculosis (silico-tuberculosis). Respiratory insufficiencies due to massive fibrosis and reduced pulmonary function, possibly with accompanying heart failure, are other potential causes of death due to silicosis.

Chronic or Ordinary Silicosis is the most common form of silicosis and can occur after many years of exposure to levels above the occupational exposure limits for airborne respirable crystalline silica dust. Not all individuals with silicosis will exhibit symptoms (signs) of the disease. Symptoms of silicosis may include (but are not limited to): Shortness of breath; difficulty breathing with or without exertion; coughing; diminished work capacity; diminished chest expansion; reduction of lung volume; heart enlargement and/or failure. It is further defined as either simple or complicated silicosis.

Simple Silicosis is characterized by lung lesions (shown as radiographic opacities) less than 1 centimeter in diameter, primarily in the upper lung zones. Often, simple silicosis is not associated with symptoms, detectable changes in lung function or disability. Simple silicosis may be progressive and may develop into complicated silicosis or progressive massive fibrosis (PMF).

SECTION XI – TOXICOLOGICAL INFORMATION, CONTD.

Complicated Silicosis or PMF is characterized by lung lesions (shown as radiographic opacities) greater than 1 centimeter in diameter. Although there may be no symptoms associated with complicated silicosis or PMF, the symptoms, if present, are shortness of breath, wheezing, cough and sputum production. Complicated silicosis or PMF may be associated with decreased lung function and may be disabling. Advanced complicated silicosis or PMF may lead to death. Advanced complicated silicosis or PMF can result in heart disease (cor pulmonale) secondary to the lung disease.

Accelerated Silicosis can occur with exposure to high concentrations of respirable crystalline silica over a relatively short period; the lung lesions can appear within five (5) years of the initial exposure. The progression can be rapid. Accelerated silicosis is similar to chronic or ordinary silicosis, except that the lung lesions appear earlier and the progression is more rapid.

Acute Silicosis can occur with exposures to very high concentrations of respirable crystalline silica over a very short time period, sometimes as short as a few months. The symptoms of acute silicosis include progressive shortness of breath, fever, cough and weight loss. Acute silicosis is a rapidly progressive, incurable lung disease and is typically fatal.

B. CANCER

IARC - The International Agency for Research on Cancer ("IARC") concluded that there is "*sufficient evidence* in humans for the carcinogenicity of crystalline silica in the form of quartz or cristobalite", there is "*sufficient evidence* in experimental animals for the carcinogenicity of quartz dust" and that there is "*limited evidence* in experimental animals for the carcinogenicity of tridymite dust and cristobalite dust." The overall IARC evaluation was that "crystalline silica inhaled in the form of quartz or cristobalite dust is *carcinogenic to humans (Group 1)*." The IARC evaluation noted that not all industrial circumstances studied evidenced carcinogenicity. The monograph also stated that "Carcinogenicity may be dependent on inherent characteristics of the crystalline silica or on external factors affecting its biological activity or distribution of its polymorphs." For further information on the IARC evaluation, see IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 100C, "Silica Dust, Crystalline, in the Form of Quartz or Cristobalite" (2012).

NTP - In its Eleventh Annual Report on Carcinogens, concluded that respirable crystalline silica is known to be a human carcinogen, based on sufficient evidence of carcinogenicity from studies in humans indicating a causal relationship between exposure to respirable crystalline silica and increased lung cancer rates in workers exposed to crystalline silica dust.

OSHA - Crystalline silica is not on the OSHA carcinogen list.

CALIFORNIA PROPOSITION 65 - Crystalline silica in October 1996 was listed on the Safe Drinking Water and Toxic Enforcement ACT of 1986 as a chemical known to the state to cause cancer or reproductive toxicity.

There have been many articles published on the carcinogenicity of crystalline silica, which the reader should consult for additional information; the following are examples of recently published articles: (1) "Dose-Response Meta-Analysis of Silica and Lung Cancer", Cancer Causes Control, (20):925-33 (2009); (2) "Occupational Silica Exposure and Lung Cancer Risk: A Review of Epidemiological Studies 1996-2005", Ann Oncol, (17) 1039-50 (2006); (3) "Lung Cancer Among Industrial Sand Workers Exposed to Crystalline Silica", Am J Epidemiol, (153) 695-703 (2001); (4) "Crystalline Silica and The Risk of Lung Cancer in The Potteries", Occup Environ Med, (55) 779-785 (1998); (5) "Is Silicosis Required for Silica-Associated Lung Cancer?", American Journal of Industrial Medicine, (37) 252- 259 (2000); (6) "Silica, Silicosis, and Lung Cancer: A Risk Assessment", American Journal of Industrial Medicine, (38) 8-18 (2000); (7) "Silica, Silicosis, and Lung Cancer: A Response to a Recent Working Group Report", Journal of Occupational and Environmental Medicine, (42) 704-720 (2000).

C. AUTOIMMUNE DISEASES

There is evidence that exposure to respirable crystalline silica (without silicosis) or that the disease silicosis may be associated with the increased incidence of several autoimmune disorders, -- scleroderma, systemic lupus erythematosus, rheumatoid arthritis and diseases affecting the kidneys. For a review of the subject, the following may be consulted: (1) "Antinuclear Antibody and Rheumatoid Factor in Silica-Exposed Workers", Arh Hig Rada Toksikol, (60) 185-90 (2009); (2) "Occupational Exposure to Crystalline Silica and Autoimmune Disease", Environmental Health Perspectives, (107) Supplement 5, 793-802 (1999); (3) "Occupational Scleroderma", Current Opinion in Rheumatology, (11) 490-494 (1999); (4) "Connective Tissue Disease and Silicosis", Am J Ind Med, (35), 375-381 (1999).

SECTION XI – TOXICOLOGICAL INFORMATION, CONTD.**D. TUBERCULOSIS**

Individuals with silicosis are at increased risk to develop pulmonary tuberculosis, if exposed to persons with tuberculosis. The following may be consulted for further information: (1) "Tuberculosis and Silicosis: Epidemiology, Diagnosis and Chemoprophylaxis", *J Bras Pneumol*, (34) 959-66 (2008); (2) *Occupational Lung Disorders*, Third Edition, Chapter 12, entitled "Silicosis and Related Diseases", Parkes, W. Raymond (1994); (3) "Risk of Pulmonary Tuberculosis Relative to Silicosis and Exposure to Silica Dust in South African Gold Miners," *Occup Environ Med*, (55) 496-502 (1998); (4) "Occupational Risk Factors for Developing Tuberculosis", *Am J Ind Med*, (30) 148-154 (1996).

E. KIDNEY DISEASE

There is evidence that exposure to respirable crystalline silica (without silicosis) or that the disease silicosis is associated with the increased incidence of kidney diseases, including end stage renal disease. For additional information on the subject, the following may be consulted: (1) "Mortality from Lung and Kidney Disease in a Cohort of North American Industrial Sand Workers: An Update", *Ann Occup Hyg*, (49) 367-73 (2005); (2) "Kidney Disease and Silicosis", *Nephron*, (85) 14-19 (2000); (3) "End Stage Renal Disease Among Ceramic Workers Exposed to Silica", *Occup Environ Med*, (56) 559-561 (1999); (4) "Kidney Disease and Arthritis in a Cohort Study of Workers Exposed to Silica", *Epidemiology*, (12) 405-412 (2001).

F. NON-MALIGNANT RESPIRATORY DISEASES

NIOSH has cited the results of studies that report an association between dusts found in various mining operations and non-malignant respiratory disease, particularly among smokers, including bronchitis, emphysema, and small airways disease. *NIOSH Hazard Review – Health Effects of Occupational Exposure to Respirable Crystalline Silica*, published in April 2002, available from NIOSH, 4676 Columbia Parkway, Cincinnati, OH 45226, or at <http://www.cdc.gov/niosh/02-129A.html>.

Respirable dust containing newly broken particles has been shown to be more hazardous to animals in laboratory tests than respirable dust containing older silica particles of similar size. Respirable silica particles which had aged for sixty days or more showed less lung injury in animals than equal exposures of respirable dust containing newly broken pieces of silica.

Aluminum Oxide:

Exposure route: Inhalation, ingestion, eye/skin contact.

Target organs: Respiratory system, gastrointestinal system, eyes, skin.

Acute effect: Inhalation or ingestion of high concentrations of this substance may cause gastrointestinal and/or upper respiratory tract irritation. Eye and skin irritant.

Chronic effect/carcinogenicity: Aluminum oxide is not classifiable as a human carcinogen. On occasion workers chronically exposed to aluminum-containing dusts or fumes have developed severe pulmonary reactions including fibrosis, emphysema and pneumothorax. Long-term exposure may have effects on the central nervous system.

Sodium Oxide:

Exposure route: Inhalation, ingestion, eye/skin contact.

Target organs: Respiratory system, gastrointestinal system, eyes, skin.

Acute effect: Corrosive – Sodium oxide reacts violently with water to form sodium hydroxide. Causes burns of skin, eyes, respiratory and gastrointestinal tracts, extremely destructive to mucous membranes.

Chronic effect/carcinogenicity: Not classifiable as human carcinogen.

Iron Oxide: (Ferric Oxide)

Exposure route: Inhalation, ingestion, skin

Target organs: Respiratory system, skin, eyes, neurological system

Acute effect: Major findings: stupor, shock, acidosis, hematemesis, bloody diarrhea or coma. Minor findings: vomiting, diarrhea, mild lethargy. Benign pneumoconiosis with X-ray shadows indistinguishable from fibrotic pneumoconiosis. Experimental work in animals exposed by intratracheal injection or by inhalation to iron oxide mixed with less than 5% silica has shown no evidence of fibrosis produced in lung tissue.

SECTION XI – TOXICOLOGICAL INFORMATION, CONTD.

Chronic effect/carcinogenicity: Irritability, nausea or vomiting, and normocytic anemia. When exposed to levels greater than 50 to 100 milligram per day, it can result in pathological deposition of iron in the body tissues causing fibrosis of the pancreas, diabetes mellitus, and liver cirrhosis. Workers exposed to iron oxide fume and silica may develop a “mixed dust pneumoconiosis.” Not classifiable as human carcinogen.

Potassium Oxide:

Exposure route: Inhalation, ingestion, eye/skin contact.

Target organs: Respiratory system, gastrointestinal system, eyes, skin.

Acute effect: Corrosive – Potassium oxide reacts violently with water to produce potassium hydroxide. If inhaled, causes sore throat, cough, burning sensation and shortness of breath. Contact with skin produces pain and blisters. Severe deep burns, redness and pain occur with eye contact. Ingestion results in burning sensations, abdominal pain, shock or collapse.

Chronic effect/carcinogenicity: Not classifiable as human carcinogen.

Calcium Oxide:

Exposure route: Inhalation, ingestion, skin/eye contact.

Target organs: Eyes, skin, respiratory system.

Acute effect: Direct contact with tissues, can result in burns and severe irritation because of its high reactivity and alkalinity. Major complaints of workers exposed to lime consist of irritation of the skin and eyes, although inflammation of the respiratory passages, ulceration and perforation of the nasal septum, and even pneumonia has been attributed to inhalation of the dust.

Chronic effect/carcinogenicity: Not classifiable as human carcinogen.

Magnesium Oxide:

Exposure route: Inhalation, eye/skin contact.

Target organs: Eyes, respiratory system.

Acute effect: Magnesium oxide dust caused slight irritation of the eyes and nose, conjunctivitis, inflammation of the mucous membrane, and coughing up discolored sputum after industrial exposures amongst workers exposed to an unspecified concentration of MgO.

Chronic effect/carcinogenicity: Not classifiable as human carcinogen.

Calcium Carbonate:

Exposure route: Inhalation, skin/eye contact.

Target organs: Eyes, skin, respiratory system.

Acute effect: Irritation of the eyes, skin and respiratory system and cough. It has been reported that there may be a silicosis risk when using impure limestone containing in excess of 3% quartz. However, it is claimed that pure calcium carbonate does not cause pneumoconiosis. Adverse health effects have generally not been reported in literature among workers using CaCO₃.

Chronic effect/carcinogenicity: Not classifiable as human carcinogen

SECTION XI – TOXICOLOGICAL INFORMATION, CONTD.**Limestone:**

Exposure Route: Eyes, skin, inhalation, ingestion.

Target Organs: Eyes, skin, respiratory system, gastrointestinal system

Acute Effect: Direct eye and skin contact with dust may cause irritation by mechanical abrasion or burning sensations, pain or blisters from corrosive/irritant effects. Dusts may irritate the nose, throat, gastrointestinal region and respiratory tract by mechanical abrasion or corrosive/irritant action. Coughing, sneezing, chest pain, shortness of breath, inflammation of mucous membrane, and flu-like fever may occur following exposures in excess of appropriate exposure limits. Small amounts (a tablespoonful) swallowed during normal handling operations are not likely to cause injury. Ingestion of large amounts may cause gastrointestinal irritation and blockage. Other conditions related to acute exposure to some of the metal oxides in limestone include stupor, shock, acidosis, abdominal pain, hematemesis, bloody diarrhea, coma, vomiting, diarrhea, mild lethargy, benign pneumoconiosis, sore throat, burning sensation, inflammation of the respiratory passages, ulceration, perforation of the nasal septum, pneumonia and conjunctivitis.

Chronic Effect: Repeated exposure to respirable dust in excess of appropriate exposure limits has caused silicosis, a progressive pneumoconiosis (lung disease) and lung cancer. Restrictive and/or obstructive lung function changes may result from chronic exposure. Chronic tobacco smoking may further increase the risk of developing chronic lung problems. On occasion workers chronically exposed to the metal oxides in limestone have developed severe pulmonary reactions, effects on the central nervous system, irritability, nausea or vomiting, normocytic anemia, fibrosis of the pancreas, diabetes mellitus, liver cirrhosis, and “mixed dust pneumoconiosis.”

Asphalt Bitumen:

Exposure route: Inhalation, ingestion, skin/eye contact.

Target organs: Eyes, skin and respiratory system

Acute effect: If product is heated or comes in contact with heated surfaces, exposure to asphalt fumes may increase. Asphalt fumes can cause ocular and respiratory irritation leading to coughing, shortness of breath, and headaches. Ingested asphalt has low toxicity however chewing of asphalt can cause gastric masses and stomach obstructions. Contact with hot asphalt can cause second and third degree burns.

Chronic effect/carcinogenicity: Not classifiable as a human carcinogen.

In the event of significant heating, thermal decomposition or a fire, various gases may be released. Use of hot mixed asphalt in paving operations may also result in the release of some of the following products. The health effects of these products are described below:

Carbon Monoxide:

Exposure route: Inhalation.

Target organs: Respiratory system, cardiovascular system, blood, central nervous system.

Acute effect: Inhalation of carbon monoxide causes cell oxidation to be inhibited which results in a reduction of the oxygen carrying capacity to all organs of the body. Resulting acute effects may include confusion, dizziness, headache, nausea, unconsciousness and weakness. High level exposures can result in death.

Chronic effect/carcinogenicity: Prolonged exposure may have effects on the nervous system and the cardiovascular system. Suspected to cause reproductive effects such as neurological problems, low birth weight, increased still births and congenital heart problems.

SECTION XI – TOXICOLOGICAL INFORMATION, CONTD.**Carbon Dioxide:**

Exposure route: Inhalation.

Target organs: Respiratory system, cardiovascular system.

Acute effect: Inhalation of carbon dioxide may cause dizziness, headache, and elevated blood pressure. Inhalation of high concentrations of this gas may cause hyperventilation and unconsciousness.

Chronic effect/carcinogenicity: Information on chronic effect of prolonged exposure to this substance is not documented.

Hydrogen Sulfide:

Exposure route: Inhalation, skin/eye contact

Target organs: Eyes, respiratory system, central nervous system.

Acute effect: Inhalation, even at small levels can cause fatigue, headache, apnea, lung edema, coma, insomnia, irritability of the eyes and respiratory system, dizziness and central nervous system effects. In some cases respiratory paralysis leading to death can occur.

Chronic effect/carcinogenicity: Prolonged exposure to this material can cause toxicosis in people exposed to large concentrations. Not classifiable as a human carcinogen.

Under certain circumstances, Hydrogen sulfide, a highly flammable and toxic gas, may be released from molten asphalt. H₂S is a colorless gas with an odor similar to rotten eggs. Odor cannot be relied on as a means of detection because the olfactory nerves (sense of smell) rapidly become insensitive to it. In addition, the H₂S odor may be masked by the general odor of hot asphalt. Low concentrations (50 – 100 ppm) of H₂S can irritate the eyes and respiratory tract, and may cause nervousness, cough, nausea, and headache. Prolonged exposure to concentrations between 250 – 600 ppm, may cause pulmonary edema (fluid in the lungs) and bronchial pneumonia. Brief exposure to concentrations above 500 ppm can cause unconsciousness and may be fatal. The OSHA PEL is 20 ppm (ceiling). The ACGIH TLV is 10 ppm with a STEL of 15 ppm. H₂S may accumulate in an enclosed space. Persons should stand upwind and avoid breathing the gas when opening hatches and dome covers.

Nitrogen Dioxide:

Exposure route: Inhalation, ingestion, skin/eye contact

Target organs: Eyes, skin, cardiovascular system and respiratory system.

Acute effect: Inhalation can cause burning of the respiratory tract, sore throat, cough, lung edema, dizziness, headache, apnea, weakness and vomiting. Contact with the skin and/or eyes will cause redness, pain and possibly severe burns. Exposure to very high concentrations may lead to death.

Chronic effect/carcinogenicity: Not classifiable as a human carcinogen. Prolonged exposure to this material may cause increased susceptibility to respiratory infection may aggravate asthma and allergic disorders.

Ozone:

Exposure routes: Inhalation, skin/eye contact.

Target organs: Eyes, skin and respiratory system.

Acute effect: Inhalation may cause irritation of the respiratory tract, cough, headache, shortness of breath, asthmatic reactions and sore throat. Contact with the eyes will result in irritation, pain and redness and may result in loss of vision. It may cause effects on the central nervous system resulting in headache and impaired vigilance and performance.

Chronic effect/carcinogenicity: Not classifiable as a human carcinogen.

SECTION XI – TOXICOLOGICAL INFORMATION, CONTD.**Sulfur Dioxide:**

Exposure route: Inhalation, skin/eye contact.

Target organs: Eyes, skin and respiratory system.

Acute effect: Inhalation may cause irritation of the respiratory tract, asthma-like reactions, reflex spasm of the larynx, cough, shortness of breath, sore throat and lung edema. It is possible that respiratory arrest may occur which can lead to death. Contact with eyes can cause irritation, redness, pain and severe burns.

Chronic effect/carcinogenicity: Not classifiable as a human carcinogen. Repeated or prolonged exposure may aggravate asthma.

Acute Toxicity Estimates for LRA – Not Available

SECTION XII – ECOLOGICAL INFORMATION

No data available for this product.

SECTION XIII – DISPOSAL CONSIDERATIONS**WASTE DISPOSAL METHOD**

Collect and reuse clean materials. Dispose of waste materials only in accordance with applicable federal, state, and local laws and regulations.

The above information applies to Martin Marietta Materials product only as sold. The product may be contaminated during use and it is the responsibility of the user to assess the appropriate disposal method in that situation.

SECTION XIV – TRANSPORT INFORMATION**DOT HAZARD CLASSIFICATION**

None

PLACARD REQUIRED

None

LABEL REQUIRED

Label as required by the OSHA Hazard Communication standard {29 CFR 1910.1200(f)}, and applicable state and local regulations.

SECTION XV – REGULATORY INFORMATION

OSHA: Crystalline Silica is not listed as a carcinogen.

SARA Title III: Section 311 and 312: Immediate health hazard and delayed health hazard.

TSCA: All components of the product appear on the EPA TSCA chemical substance inventory.

RCRA: Crystalline silica (quartz) is not classified as a hazardous waste under the Resource Conservation and Recovery Act, or its regulations, 40 CFR §261 et seq.

CERCLA: Crystalline silica (quartz) is not classified as a hazardous substance under regulations of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), 40 CFR §302.4

EPCRA (Emergency Planning and Community Right to Know Act): Crystalline silica (quartz) is not an extremely hazardous substance under regulations of the Emergency Planning and Community Right to Know Act, 40 CFR Part 355, Appendices A and B and is not a toxic chemical subject to the requirements of Section 313.

Clean Air Act: Crystalline silica (quartz) mined and processed by Martin Marietta Materials was not processed with or does not contain any Class I or Class II ozone depleting substances.

FDA: Silica is included in the list of substances that may be included in coatings used in food contact surfaces, 21 CFR §175.300(b)(3). (The FDA standard primarily applies to products containing silica used in the coatings of food contact surfaces).

California Proposition 65: Respirable crystalline silica is classified as a substance known to the state of California to be a carcinogen.

Massachusetts Toxic Use Reduction Act: Respirable crystalline silica is considered toxic per the Massachusetts Toxic Use Reduction Act when used in abrasive blasting and molding.

Pennsylvania Worker and Community Right to Know Act: Quartz is considered hazardous for purposes of the Act, but it is not a special hazardous substance or an environmental hazardous substance.

SECTION XVI – OTHER INFORMATION**DEFINITIONS OF ACRONYMS/ABBREVIATIONS**

ACGIH: American Conference of Governmental Industrial Hygienists

ANSI: American National Standards Institute

APF: Assigned Protection Factor

California REL: California Inhalation Reference Exposure Limit

CAS: Chemical Abstracts Service

CERCLA: Comprehensive Environmental Response, Compensation and Liability Act

CFR: US Code of Federal Regulations

DHHS: Department of Health and Human Services

EPA: Environmental Protection Agency

EPCRA: Emergency Planning and Community Right to Know Act

FDA: Food and Drug Administration

GHS: Globally Harmonized System

HEPA: High-Efficiency Particulate Air

IARC: International Agency for Research on Cancer

IDLH: Immediately Dangerous to Life and Health

LRA: Limestone Rock Asphalt

MSHA: Mine Safety and Health Administration

NIOSH: National Institute for Occupational Safety and Health, US Department of Health and Human Services

NIOSH REL: NIOSH Recommended Exposure Limit

NTP: National Toxicology Program

OEL: Occupational Exposure Limit

OSHA: Occupational Safety and Health Administration, US Department of Labor

PEL: Permissible Exposure Limit

PMF: Progressive Massive Fibrosis

RCRA: Resource Conservation and Recovery Act

SARA Title III: Title III of the Superfund Amendments and Reauthorization Act, 1986

SDS: Safety Data Sheet

STOT: Specific Target Organ Toxicity

TLV: Threshold Limit Value

TSCA: Toxic Substance Control Act

TWA: Time-Weighted Average

SECTION XVI – OTHER INFORMATION, CONTD.

User's Responsibility: The OSHA Hazard Communication Standard 29 CFR 1910.1200 requires that this SDS be made available to your employees who handle or may be exposed to this product. Educate and train your employees regarding applicable precautions. Instruct your employees to handle this product properly.

Disclaimer: The information contained in this document applies to this specific material as supplied and Martin Marietta Materials believes that the information contained in this SDS is accurate. The suggested precautions and recommendations are based on recognized good work practices and experience as of the date of publication. They are not necessarily all-inclusive or fully adequate in every circumstance as not all use circumstances can be anticipated. It may not be valid for this material if it is used in combination with other materials. It is the user's responsibility to satisfy oneself as to the suitability and completeness of this information for one's own particular use. Since the actual use of the product described herein is beyond our control, Martin Marietta Materials, assumes no liability arising out of the use of the product by others. Appropriate warnings and safe handling procedures should be provided to handlers and users. Also, the suggestions should not be confused with nor followed in violation of applicable laws, regulation, rules or insurance requirement. However, product must not be used in a manner which could result in harm.

An electronic version of this SDS is available at www.martinmarietta.com. More information on the effects of crystalline silica exposure may be obtained from OSHA (phone number: 1-800-321-OSHA; website: <http://www.osha.gov>) or from NIOSH (phone number: 1-800-35-NIOSH; website: <http://www.cdc.gov/niosh>).

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