# Mixed zinc cadmium sulfides and selenides: Human health tier II assessment

**18 September 2014**



## Chemicals in this assessment

| Chemical Name in the Inventory | CAS Number |
|---|---|
| **Cadmium selenide (CdSe)** | 1306-24-7 |
| **Cadmium selenide sulfide, (Cd2SeS)** | 12214-12-9 |
| **C.I. Pigment Yellow 35** | 8048-07-5 |
| **Cadmium selenide sulfide, (CdSeS)** | 11112-63-3 |
| **Cadmium zinc sulfide, (CdZnS)** | 12442-27-2 |
| **Cadmium selenide sulfide** | 12626-36-7 |
| **C.I. Pigment Orange 20** | 12656-57-4 |
| **C.I. Pigment Red 108** | 58339-34-7 |
| **Cadmium sulfide (CdS), solid solution with zinc sulfide, copper chloride doped** | 68512-49-2 |
| **Cadmium sulfide (CdS), solid solution with zinc sulfide, silver chloride doped** | 68583-45-9 |

# Preface

This assessment was carried out by staff of the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) using the Inventory Multi-tiered Assessment and Prioritisation (IMAP) framework.

The IMAP framework addresses the human health and environmental impacts of previously unassessed industrial chemicals listed on the Australian Inventory of Chemical Substances (the Inventory).

The framework was developed with significant input from stakeholders and provides a more rapid, flexible and transparent approach for the assessment of chemicals listed on the Inventory.

Stage One of the implementation of this framework, which lasted four years from 1 July 2012, examined 3000 chemicals meeting characteristics identified by stakeholders as needing priority assessment. This included chemicals for which NICNAS already held exposure information, chemicals identified as a concern or for which regulatory action had been taken overseas, and chemicals detected in international studies analysing chemicals present in babies' umbilical cord blood.

Stage Two of IMAP began in July 2016. We are continuing to assess chemicals on the Inventory, including chemicals identified as a concern for which action has been taken overseas and chemicals that can be rapidly identified and assessed by using Stage One information. We are also continuing to publish information for chemicals on the Inventory that pose a low risk to human health or the environment or both. This work provides efficiencies and enables us to identify higher risk chemicals requiring assessment.

The IMAP framework is a science and risk-based model designed to align the assessment effort with the human health and environmental impacts of chemicals. It has three tiers of assessment, with the assessment effort increasing with each tier. The Tier I assessment is a high throughput approach using tabulated electronic data. The Tier II assessment is an evaluation of risk on a substance-by-substance or chemical category-by-category basis. Tier III assessments are conducted to address specific concerns that could not be resolved during the Tier II assessment.

These assessments are carried out by staff employed by the Australian Government Department of Health and the Australian Government Department of the Environment and Energy. The human health and environment risk assessments are conducted and published separately, using information available at the time, and may be undertaken at different tiers.

This chemical or group of chemicals are being assessed at Tier II because the Tier I assessment indicated that it needed further investigation.

For more detail on this program please visit:**www.nicnas.gov.au**

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ACRONYMS & ABBREVIATIONS

# Grouping Rationale

This group consists of cadmium zinc sulfides, cadmium selenides and cadmium sulfoselenides. These chemicals are insoluble in water and are primarily used as stable inorganic pigments in industrial applications. The majority of these pigments have variable composition with cadmium sulfide as an end member of the series.

Cadmium zinc sulfide (CdZnS) (CAS No. 12442-27-2) is reportedly formed when CdS and ZnS are sintered together through heating, forming a crystalline lattice structure. During the production process, increasing the zinc content of CdZnS produces

lighter yellow pigments (Buxbaum and Pfaff, 2005).

Certain chemicals characterised with a Colour Index (CI) number are also included in this group since it was identified that they were composed of either cadmium sulfoselenide, cadmium zinc sulfide, or cadmium sulfide pigments. For example, pigment orange 20 (CI 77202; CAS No. 12656-57-4) and pigment red 108 (CI 77202; CAS No. 58339-34-7) are cadmium sulfoselenides. They are synthesised when sulfur is replaced by selenium in the cadmium sulfide lattice. Increasing the selenium content changes the color from orange to red (Buxbaum and Pfaff, 2005). Pigment yellow 35 (CI 77205; CAS No. 68859-25-6) is composed of crystals of cadmium sulfide and zinc sulfide where the desired hue is achieved by altering the ratio of the two components (Koleske, 2012). While available information indicates that commercial grades of these CI pigments are engineered to have low cadmium bioavailability, it is not possible to ascertain that this applies to all instances of these chemicals.

Solid solutions of CdZnS doped with metal chlorides such as those of copper (CAS No. 68512-49-2) or silver (CAS No. 68583-45-9) are also included in this group. Copper or silver were reported as luminescence activators at concentrations of up to 100 ppm (National Academy of Science, 1997). Copper is an essential mineral with a recommended upper intake level of up to 10 mg/day (NHMRC, 2006) while the total lifetime oral NOAEL for silver is 10 g (WHO, 2003). Given the presence of low levels of copper and silver in doped CdZnS solutions, it is expected that health effects from oral exposure to these compounds would be related to CdZnS and the effects of copper and silver would be considered to be negligible compared with cadmium. Thus, these chemicals are also included in this group assessment.

# Import, Manufacture and Use

## Australian

Cadmium selenosulfide pigments were reported to be manufactured in Australia (De Silva & Donnan, 1981).

## International

The following individual cadmium compounds have international uses from European Union Registration, Evaluation and Authorisation of Chemicals (EU REACH) dossiers; Galleria Chemica, and the US National Library of Medicine's Hazardous Substances Data Bank (HSDB).

***Cadmium selenide, CdSe* (CAS No. 1306-24-7)** has been reported to have the following uses:

Commercial use including:

- as a component of pigments in paints, especially in artists' paint colours;
- as stabilisers in colouring textiles, paper, rubber, plastics, glasses, and ceramic glazes;
- constituent in firework formulation.

Site-limited use including:

- semiconducting component in photoconverting cells, light amplifiers, radiation detectors, thin film transistors and diodes.

***Cadmium zinc sulfide, CdZnS* (CAS No. 8048-07-5)** has been reported to have the following uses:

Domestic use including:

- as a component in professional artists' paint colours.

Site-limited use including:

- in the manufacture of colour and enamel for ceramic, glass, and metal decorations.
- as a pigment in polymers during high-temperature processing.

CdZnS was also used as a tracer for chemical and biological warfare agents (National Academy of Sciences, 1997).

***C.I. Pigment Orange 20*** **(CAS No. 12656-57-4),** ***C.I. Pigment yellow 35*** **(CAS No. 8048-07-5)** and ***C.I. Pigment Red 108*** **(CAS No. 58339-34-7)** have one or more of the following uses:

Domestic use including:

- as a component in artists' paints, glass, ceramic and plastics, including use in safety applications (ECHA, 2012).

No international industrial uses were identified for solid solutions of CdZnS doped with metal chlorides such as copper (CAS No. 68512-49-2) or silver (CAS No. 68583-45-9).

# Restrictions

## Australian

Cadmium and cadmium compounds are listed in the Poisons Standard (the Standard for the Uniform Scheduling of Medicines and Poisons—SUSMP (SUSMP, 2013)) under the following Schedules:

***Appendix I, The uniform paint standard***

The following applies to paints containing cadmium or cadmium compounds at >0.1 % (the proportion of a substance for the purposes of this Schedule is calculated as a percentage of the element present in the non-volatile content of the paint).

'A person must not manufacture, sell, supply or use a paint containing >0.1 % of cadmium or cadmium compounds for application to:

- a roof or any surface to be used for the collection or storage of potable water; or
- furniture; or
- any fence, wall, post, gate or building (interior or exterior) other than a building which is used exclusively for industrial purposes or mining or any oil terminal; or
- any premises used for the manufacture, processing, preparation, packing or serving of products intended for human or animal consumption' (SUSMP, 2013).

Additionally, 'a person must not manufacture, sell, supply or use a paint for application to toys unless the paint complies with the specification for coating materials contained in Australian/New Zealand Standard AS/NZS ISO 8124.3:2012 entitled *Safety of toys Part 3: Migration of certain elements* (ISO 8124-03:2010, MOD)' (SUSMP, 2013).

***'Schedule 6*** except when:

(a) included in Schedule 4; or

(b) in paints or tinters containing 0.1 per cent or less of cadmium calculated on the non-volatile content of the paint or tinter' (SUSMP, 2013).

Schedule 6 substances are considered to have 'moderate potential for causing harm, the extent of which can be reduced through the use of distinctive packaging with strong warnings and safety directions on the label' (SUSMP, 2013).

Cadmium and its compounds are also listed as restricted hazardous chemicals in the Australian Work Health and Safety Regulations 2011 for 'use in abrasive blasting at a concentration of greater than 0.1 % as cadmium' (SafeWork Australia).

## International

Cadmium and cadmium compounds are listed on the following (Galleria Chemica):

- EU Cosmetic Directive 76/768/EEC Annex II: List of Substances which must not form part of the composition of cosmetic products;
- New Zealand Cosmetic Products Group Standard—Schedule 4: Components cosmetic products must not contain; and
- Health Canada List of prohibited and restricted cosmetic ingredients (The "Hotlist").

Cadmium compounds (as Cd) cannot be used in substances and preparations placed on the market for sale at the following concentrations in:

- synthetic organic polymers, as listed in the European Commission Regulation (EU) No 835/2012, > 0.01 % by weight of the plastic material;
- paints with a zinc content of >10% by weight of the paint ≥0.1% by weight;
- metal plating; and
- brazing (soldering/welding) fillers ≥0.01% by weight.

# Existing Worker Health and Safety Controls

## Hazard Classification

Cadmium compounds not individually listed on the HSIS are, by default, covered by a generic 'cadmium compounds' classification (Safe Work Australia) as hazardous with the following risk phrase for human health.

Xn; R20/21/22: Harmful by inhalation, in contact with skin and if swallowed.

However, it is specified that cadmium sulfoselenide (xCdS.yCdSe), mixtures of cadmium sulphide with zinc sulphide (xCdS.yZnS), and mixtures of cadmium sulphide with mercury sulphide (xCdS.yHgS) are exceptions to the 'generic' cadmium classification (Safe Work Australia).

As a 'worst case', the HSIS classification for cadmium sulfide will also be considered in classifying the cadmium compounds in this group. Cadmium sulfide has similar characteristics to the cadmium compounds in this group such that they are insoluble in aqueous solution and expected not to be readily bioavailable. Based on the toxicity data for cadmium sulfide, its bioavailability is sufficient to cause significant toxic effects (NICNASb). The calcined pigments (pigment yellow 35, pigment orange 20, and pigment red 108) are stated to have very low bioavailability and, in cases where this can be demonstrated, some or all of the classifications derived from cadmium sulfide may not apply.

Cadmium sulfide is classified as hazardous, with the following risk phrases for human health in the HSIS (Worksafe Australia):

Carc. Cat. 2; R45 - May cause cancer.

Muta. Cat. 3; R68 - Possible risk of irreversible effects.

Repr. Cat. 3; R62 - Possible risk of impaired fertility.

Repr. Cat. 3; R63 - Possible risk of harm to the unborn child.

T; R48/23/25 - Toxic: danger of serious damage to health by prolonged exposure. through inhalation and if swallowed.

Xn; R22- Harmful if swallowed.

## Exposure Standards

### Australian

Cadmium and cadmium compounds have an exposure standard of 0.01 mg/m$^3$ time weighted average (TWA) (Safe Work Australia).

### International

For cadmium and cadmium compounds, the following exposure limits were identified (Galleria Chemica).

An exposure limit (TWA) of 0.01–0.2 mg/m$^3$ in different countries such as Canada, USA, Latvia and Switzerland.

# Health Hazard Information

While there are limited data available on these specific chemicals, data sources for determining their hazard include animal studies on well characterised insoluble cadmium compounds such as cadmium oxide and cadmium sulfide, and a large amount of literature on observations of cadmium exposure in humans. The toxicity data for cadmium chloride and cadmium sulfate by the oral route (NICNASa; NICNASb) are considered relevant to the chronic systemic toxicity of cadmium compounds in this group. The extent to which these data are quantitatively relevant will depend on the bioavailability of the pigments in this group at gastric pH.

## Toxicokinetics

The following bioaccessibility values for the calcinated form of certain compounds were submitted to NICNAS. For CI Pigment Red 108 (CdSSe): gastric bioaccessibility = 0.69 ± 0.07 (expressed as % released Cd from the total Cd content in two hours); interstitial bioaccessibility = 0.002–0.004 (expressed as % released Cd from the total Cd content in 24–168 hours); lysosomal bioaccessibility = <0.00008–0.005 (expressed as % released Cd from the total Cd content in 24–168 hours); and, sweat bioaccessibility = 0.02–0.06 (expressed as % released Cd from the total Cd content in 24–168 hours). For CI Pigment Yellow 35 (CdZnS): gastric bioaccessibility = 0.70 ± 0.09 (expressed as % released Cd from the total Cd content in two hours); interstitial bioaccessibility = 0.0002-–0.0002 (expressed as % released Cd from the total Cd content in 24–168 hours); lysosomal bioaccessibility = <0.00008 – <0.00008 (expressed as % released Cd from the total Cd content in 24–168 hours); and, sweat bioaccessibility = 0.007 – 0.008 (expressed as % released Cd from the total Cd content in 24–168 hours) (N. Lombaert, personal communication, 18 June 2015)

Furthermore, a previous study in rats has shown that absorption of calcined cadmium red (CI Pigment Red 108) and cadmium yellow (CI Pigment Yellow 35) through the respiratory route was very low in comparison to cadmium fume and cadmium carbonate-exposed groups (Rusch et al., 1986). Blood levels of cadmium in the cadmium red and cadmium yellow-exposed groups were comparable to controls (Rusch et al., 1986). However, the study may not represent uncalcined cadmium pigments, which are expected to have differing bioavailability and extractability compared with calcined pigments. In this instance, any cadmium released from these chemicals (calcinated and uncalcined) is relevant to the assessment of these cadmium compounds.

The chemicals in this group are considered to be water-insoluble. Cadmium oxide is reported to be relatively water-insoluble but may dissolve at gastric pH, thus may have similar absorption and toxicity to soluble cadmium compounds. While the compounds in this group are expected to have lower acid solubility than cadmium oxide, liberated cadmium ions will act similarly regardless of their source compound. In addition, it was reported that cadmium sulfide, cadmium carbonate, and cadmium oxide (water-insoluble cadmium compounds) can be changed to water-soluble cadmium salts by interaction with acids or light and oxygen (ATDSR).

*Animal studies*

In rodent dietary exposure studies using cadmium oxide, absorption fractions following oral exposure to low doses of cadmium oxide were reported to be much greater than those determined for exposure to higher doses. Significant accumulation of cadmium was detected in the liver, kidneys, lungs and spleen. Levels in the liver and kidneys were reported to be dose-dependent. However, no significant increases in blood or urine levels of cadmium were detected. (EU RAR, 2007).

Animal studies have demonstrated that absorption of cadmium oxide following inhalation exposure ranges from 30 % (dusts—size-dependent) to 50 % (fumes). In humans, inhalation absorption of 10–30 % (dusts, size-dependent) was reported (OECD, 2004). Dermal absorption is expected to be low due to the ionic nature of the chemical.

*Human studies*

A large amount of information on the toxicokinetics of the cadmium ion in humans is available. This information is mostly related to general cadmium exposure in workers, and is not specific to particular cadmium compounds.

Human data available on cadmium indicate that gastro-intestinal absorption is low (5–10 %), and varies depending on the source of the cadmium, presence of zinc in the diet, the body's iron stores (deficiencies are linked with increased cadmium absorption) and the person's age and physiological condition (young or pregnant or lactating animals have been shown to absorb more cadmium than non-pregnant adult animals) (EU RAR, 2007; OECD, 2004).

Following long-term low-level exposure, cadmium is reported to be widely distributed in the body and has a biological half-life of 10–20 years. The greatest accumulation occurs in the kidneys and liver, with only 0.005–0.02 % reported to be excreted in urine and faeces each day. Cadmium is also detectable in the placenta, and can cross the placental barrier, although foetal concentrations are lower than placental concentrations. Concentrations of cadmium in newborn blood were 40–50 % lower than the levels in maternal blood (EU RAR, 2007). Cadmium is reported to be found in human breast milk at <1 µg/L (OECD, 2004). In tissue, cadmium is bound to metallothionein, a low molecular weight metal-binding protein thought to play a key role in metabolising and detoxifying cadmium (EU RAR, 2007).

It should be noted that higher levels of cadmium (particularly in the kidney) are detected in smokers compared with non-smokers, as cadmium has been shown to accumulate in tobacco plant leaves (WHO, 2010).

## Acute Toxicity

### Oral

The compounds in this group, apart from CdSe (CAS No. 1306-24-7), meet the exemption from the generic 'cadmium compounds' hazard classification with the risk phrase 'Harmful if swallowed' (Xn; R22) in HSIS (see **Hazard Classification**) (Safe Work Australia). While there are limited data available for these specific chemicals, data from insoluble cadmium compounds (cadmium sulfide and cadmium oxide), indicate this classification will vary in its application to the compounds in this group depending on the bioavailability of the individual grade of the chemical.

It was reported that the LD50 values for a form of cadmium sulfoselenide in mice ranged from 1623–2425 mg Cd/kg (>2000 mg/kg based on cadmium sulfoselenide) (Vorob'eva & Shabalina, 1975; Vorob'eva & Shabalina, 1978). From these same studies, the LD50 of cadmium sulfide was also reported to be in the range of 907-1166 mg/kg in mice with effects including dystrophic changes in the heart, liver and kidneys as well as local necrosis of the gastrointestinal mucosa.

Cadmium oxide was reported to be acutely toxic in rats following oral exposure, with oral LD50 values in the range 72–296 mg/kg bw (EU RAR, 2007; NICNASa). The differences in the LD50 values among the compounds may be considered to indicate the difference in availability of cadmium ions between these compounds.

### Dermal

The compounds in this group, apart from CdSe (CAS No. 1306-24-7), meet the exemption from the generic 'cadmium compounds' hazard classification with the risk phrase 'Harmful in contact with skin' (Xn; R21) in HSIS (see **Hazard Classification**) (Safe Work Australia).

There are no experimental dermal toxicity data available for these specific chemicals; dermal absorption is expected to be low due to the ionic nature of the compounds in this group. The chemicals in this group are expected to behave similarly to cadmium oxide and cadmium sulfide which do not have acute dermal classification.

### Inhalation

The compounds in this group, apart from CdSe (CAS No. 1306-24-7) meet the exemption from the generic 'cadmium compounds' hazard classification with the risk phrase 'Harmful if inhaled' (Xn; R20) in HSIS (Safe Work Australia).

There are limited data available for these specific chemicals. The chemicals in this group are expected to behave similarly to cadmium sulfide, which has similar chemical composition, and which does not have an acute inhalation classification.

Sprague Dawley (SD) rats (26 animals/sex/dose) were exposed to aerosolized cadmium red (equivalent to cadmium sulfoselenide) and cadmium yellow (equivalent to cadmium zinc sulfide) at concentrations of approximately 100 mg Cd/$m^3$ for 2 hours. No mortalities were observed in either chemical group. For both chemicals, excessive lacrimation was observed 4-hours post-exposure. In addition, there was also a higher incidence of kidney discolouration in the cadmium red group compared to the controls or cadmium yellow group. The LC50 value for both chemicals was determined to be > 100 mg/$m^3$ (Rusch et al., 1986; REACH).

In a non-guideline experiment, CdZnS (5.0 mg in 0.5 mL saline solution) was administered to anaesthetised male Fischer 344 (F344) rats (30 animals/group) by intratracheal instillation. Ten animals were sacrificed for bronchoalveolar lavage fluid (BALF) and histopathology on day 1, week 1, and week 14 after dosing with CdZnS. The animals showed signs of dyspnoea and lethargy, which were reversible within 1 hour. At day 1 post-treatment, the following parameters were found to be significantly higher in the CdZnS group compared with the control group: alkaline and acid phosphatases, mean protein level, β-glucuronidase, and white blood cell (WBC) and macrophage count. High levels of Cd and Zn in the blood and liver were also reported. High concentrations of Cd and Zn were found in the lung; these declined over the post-treatment period. At week 14 post-treatment, statistically significant amounts of Cd and Zn were found in the kidney. Histopathology on the CdZnS group showed interstitial inflammation of the trachea that consisted of lymphocyte and neutrophil infiltration in the mucosa and submucosal tissues. The study concluded that intratracheal instillation of CdZnS causes an acute inflammatory response in the lungs and that the bioavailability of CdZnS was poor as evidenced by the small amount found in the kidneys (Bergmann et al., 2000).

Intratracheal administration of cadmium sulfoselenide (15 mg/animal) in rats caused pneumonia, pneumosclerosis, and lung emphysema (Vorob'eva & Shabalina, 1975; Vorob'eva & Shabalina, 1978).

### Observation in humans

Several cases of cadmium poisoning (compound not specified) as a result of ingesting contaminated food or drinks have been documented. Reported signs and symptoms of toxicity include nausea, vomiting, diarrhoea and abdominal cramps.

There are many case studies of acute poisoning following inhalation of cadmium oxide fumes, or fumes produced by heating cadmium-containing materials to high temperatures. Documented signs of toxicity include nausea, fever, difficulties in respiration and severe respiratory irritation. Pulmonary oedema, resulting in mortality, was commonly reported following acute exposure (EU RAR, 2007).

## Corrosion / Irritation

### Respiratory Irritation

While limited data are available to indicate mild irritation effects from CdZnS exposure (see **Acute Toxicity - Inhalation**), based on the sublethal symptoms observed in inhalation studies in animals and observations in humans from exposure to cadmium compounds, the chemicals in this group are expected to be irritating to the respiratory tract.

### Skin Irritation

No dermal effects were observed when CdZnS was intradermally applied to rabbits at a dose of 9.4 g/kg for 24 hours (National Academy of Sciences, 1997).

### Eye Irritation

Rabbits treated with a mixture containing approximately 35 % CdZnS by instillation showed negligible corneal effects. (National Academy of Sciences, 1997).

## Sensitisation

### Skin Sensitisation

While there are no experimental data that are available for any chemicals in this group, data from observations in humans have shown dermal effects when cadmium sulfide, based on its use in tattoo inks, is exposed to light (see **Observations in humans**). However, there is insufficient evidence to warrant classifying cadmium sulfide or any chemicals in this group as a skin sensitiser.

### Observation in humans

Cadmium sulfide was historically been used as the main constituent of yellow pigments used in tattooing. In a 1962 report, case studies on humans who were tattooed using cadmium sulfide pigments showed localised skin swellings around the tattooed skin upon exposure to sunlight (Tindall & Smith, 1962).

In an experiment conducted on human skin, the chemical was applied as a tattoo and exposed to different wavelengths of light. It was shown that swelling, lasting 2–72 hours, appeared when the skin was exposed to wavelengths of 380–450 nm. Histological examination of skin biopsies from the application site revealed slightly dilated capillaries surrounded by sparse infiltrates of lymphocytes. However, a negative result was found in a patch test where the chemical was superficially applied to skin for 48 hours and subsequently irradiated with identical wavelengths of light (Bjornberg, 1963).

## Repeated Dose Toxicity

### Oral

While limited data are available for the specific cadmium compounds in this group, data from animal studies and observations in humans following oral exposure to soluble cadmium salts (cadmium chloride and cadmium sulfate) are provided below as read-across. It is expected that in a 'worst-case' scenario, oral exposure to any of the chemicals in this group would release bioavailable cadmium ions at gastric pH (see **Toxicokinetics**). While these chemicals are not classified for this endpoint, the analogue cadmium sulfide is classified as hazardous with the risk phrase 'Toxic: danger of serious damage to health by prolonged exposure if swallowed.' (T; R48/25) in HSIS (Safe Work Australia).

In an experiment conducted in SD rats (10 animals/sex/group), cadmium selenide was orally administered at doses of 30, 300, and 1000 mg/kg per day, for 28 days. No mortalities, clinical signs, or differences in body weight were observed in any group at the end of the study. Histopathological examination revealed no effects related to chemical treatment except for one case of focal hepatic inflammation in the high dose group. The NOAEL in this study was determined to be > 1000 mg/kg/d for both sexes in rats (Kim et al, 2009).

A chronic oral exposure study in male Wistar rats using cadmium chloride administered via drinking water (1, 5, 50 mg/L, calculated daily dose ranges were 0.049–0.223, 0.238–0.977, and 2.073–10.445 mg/kg bw/day, respectively), over 12 months, reported no treatment related signs at 1 mg/L. At ≥5 mg/L, increased lumbar spine deformities and a decrease in lumbar spine mineralisation (including calcium, magnesium, zinc, copper, iron and phosphate) were reported. Decreased mechanical strength of the vertebral column at the fourth lumbar vertebra (L4) was reported at 50 mg/L. The NOAEL (no observed adverse effect level) and LOAEL (lowest observed adverse effect level) for this study were reported to be 0.2 mg/kg bw/day and 0.5 mg/kg bw/day, respectively (ATSDR; NICNASb).

Cadmium salts (cadmium chloride and cadmium sulfate) are classified as hazardous, with the risk phrase 'Toxic: danger of serious damage to health by prolonged exposure if swallowed' (T; R48/R25) in HSIS (Safe Work Australia). Based on the available data on repeat oral exposure, there is sufficient evidence from animal studies and observations in humans to warrant this classification applying to the compounds in this group, unless bioavailability by this route can be demonstrated to be very low.

### Dermal

No data are available.

### Inhalation

While there are no data available for specific cadmium compounds in this group, adverse effects from animals exposed by repeat inhalation to cadmium sulfide and observations in humans exposed to cadmium oxide are provided as read across. Information from cadmium telluride (CdTe) is also included to complement the data of cadmium sulfide.

In an experiment conducted on Han:NMRI mice (48 females/dose/group), cadmium sulfide was administered by inhalation at concentrations of 90, 270, or 1000 µg/m$^3$ for eight or 19 hours/day, five days/week, for 69 weeks. The mass median aerodynamic diameter (measurement of chemical particle size) of cadmium sulfide was reported to be 0.2−0.6 µm (geometric standard deviation of 1.6). The survival rates of animals in the 90 and 270 µg/m$^3$ groups were similar to controls. Effects that were observed include alveolar enlargement, thickening and scarring of the lung tissues, and tumours of the trachea. These effects were also observed in an experiment conducted on Hoe:SYHK hamsters at the same doses of cadmium sulfide (IARC, 1993).

Exposure to CdTe in the form of a dry aerosol to Wistar rats for up to 28 consecutive days at concentration levels of 0.003, 0.01, 0.03 and 0.09 mg/L was associated with adverse effects. The associated adverse effects at the lowest tested concentration were slight, transient tachypnoea during the last week of the exposure, increase in lungs weights (by about 1.5-2 times), which correlated with minimal alveolar/interstitial/bronchiolar inflammation and minimal hyperplasia of the Type II pneumocytes. As adverse effects on the respiratory tract were observed at the lowest possible concentration (0.003 mg/L achieved by 2 hours exposure session to 0.01 mg/L), a lowest observed adverse effect concentration (LOAEC) value of 3 mg/m$^3$ could be set but a no observed adverse effect level (NOAEL) could not be determined in this study (REACH CdTe).

Cadmium sulfide is classified as hazardous, with the risk phrase 'Toxic: danger of serious damage to health by prolonged exposure through inhalation' (T; R48/R23) in HSIS (Safe Work Australia). Based on the available data on repeat inhalation exposure, there is sufficient evidence from animal studies and observations in humans to warrant this classification applying to the compounds in this group, unless bioavailability by this route can be demonstrated to be very low.

### Observation in humans

Exposure to low levels of cadmium over a long period of time has been linked to chronic cadmium poisoning. The effects of cadmium on specific target organs following exposure in humans are summarised below.

***Respiratory effects***

There are a number of documented case studies of workers chronically exposed to fumes of cadmium oxide (EU RAR, 2007). Effects reported included fatigue, respiratory irritation, shortness of breath, decreased lung function and recurrent bronchitis.

It is suggested that an increase in residual levels of cadmium oxide in lungs may lead to chronic obstructive airway disease and (in some cases) mortality, all of which have been documented following exposure (EU RAR, 2007). A lowest observed adverse effect concentration (LOAEC) of 0.0031 mg/L, based on lung effects (increased residual levels of the cadmium oxide), was derived from a study on workers exposed to the fumes of cadmium oxide at <0.5 mg/m$^3$ over several years.

***Renal effects***

The kidneys are considered to be the main target organ for cadmium toxicity following repeated oral or inhalation exposure (EU RAR, 2007; ATSDR, 2012). Initial signs of kidney effects following cadmium exposure include tubular dysfunction, decreased glomerular filtration rate, and increased proteinuria and enzymuria. Renal dysfunction is considered to occur when renal cortex cadmium concentrations reach 200 ppm (equivalent to 5–10 µg Cd/g creatinine) (EU RAR, 2007).

Increased incidence of kidney stones has also been reported in workers exposed to cadmium (18 %), compared with unexposed workers (3 %) (EU RAR, 2007).

***Skeletal effects***

Oral exposure is reported to cause bone disease in humans (EU RAR, 2008). While the underlying mechanism is not clearly understood, it is thought that cadmium-induced kidney damage and the resulting hypercalcinuria (elevated levels of calcium in the urine) may promote osteoporotic effects in bone (EU RAR, 2007).

In a case study in Japan, a high incidence of Itai-Itai disease was diagnosed in patients from specific geographical locations. It was found that farms in these areas were irrigated by a river being polluted by cadmium sludge from an upstream mine, and the patients may have been exposed to cadmium for over 30 years. Samples of rice taken from those areas were reported to contain cadmium at 0.68 mg/kg, compared with 0.066 mg/kg in other areas (EU RAR, 2007). Itai-Itai disease is characterised by osteomalacia (softening of the bones), osteoporosis, severe renal tubular disease, and is associated with severe pain (WHO, 2011). A limited number of case reports have also documented clinical bone disease in workers exposed to cadmium compounds (EU RAR, 2007).

## Genotoxicity

While there are no data available for specific cadmium compounds in this group, the available data from cadmium sulfide and results for other cadmium compounds indicate that absorbed cadmium is a possible mutagen.

***Cadmium sulfide***

Cadmium sulfide was reported to induce DNA strand breaks in Chinese hamster ovary (CHO) cells and chromosome aberrations in human lymphocytes in vitro (IARC, 1993; REACH).

***Other cadmium compounds***

Cadmium salts (not specified) have been shown to induce genotoxic effects in both in vitro (reduction in colony-forming ability and DNA strand breaks in *Escherichia coli*) and in vivo studies (sister chromatid exchange and chromosomal aberration in mice, and DNA strand breaks in rats) (EU RAR, 2007; IARC, 2012).

***Observations in humans***

Chromosomal aberrations, increased frequency of micronuclei, and sister chromatid exchanges have been detected in humans environmentally exposed to cadmium (EU RAR, 2007). However, the specific cadmium compounds involved are not identified.

Cadmium sulfide is classified as hazardous, Category 3 mutagens, with the risk phrase ‘Possible risk of irreversible effects’ (Xn; R68) in HSIS (Safe Work Australia). Based on the available data, there is sufficient evidence from animal studies and observations in humans to warrant this classification applying to the compounds in this group unless bioavailability by all routes of exposure can be demonstrated to be very low.

## Carcinogenicity

While there are no data available for any chemicals in this group, the available data from cadmium sulfide and observations in humans indicate that cadmium has carcinogenic potential.

In an experiment conducted on Wistar rats (20–40 males or 20 females per dose group), cadmium sulfide was administered by inhalation at doses of 90, 270, 810, or 2430 µg/m$^3$ for 22 hours/day, seven days a week, for 18 months. The incidence of primary pulmonary tumours was increased in all dose groups compared with the controls. The observed tumours were mostly adenomas, adenocarcinomas, bronchioalveolar adenomas, and squamous-cell carcinomas (IARC, 1993; REACH CdS).

In another experiment, intratracheal administration of cadmium sulfide in Wistar rats (40 females/dose) at doses of 630, 2500, or 10 000 µg induced dose-related increase in the incidence of lung tumours, primarily adenocarcinomas (IARC, 1993).

It was also shown that subcutaneous injections of 10 % aqueous suspension (25 mg cadmium sulfide suspended in 0.25 mL saline) in both sides of the dorsal midline of Wistar rats induced fibrosarcomas at the site of injection. The same effect was observed upon intramuscular injections of 10 % aqueous suspension (50 mg cadmium sulfide suspended in 0.5 mL saline) (IARC, 1993; REACH CdS).

***Observations in humans***

There are many case studies that explore the link between exposure to cadmium and increased incidence of cancer in workers (NTP, 2011; IARC, 2012).

The International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as ‘Carcinogenic to humans (Group 1)’ based on sufficient evidence in humans and experimental animals (IARC, 2012). Additionally, the US National Toxicology Program (NTP) has also classified cadmium and cadmium compounds as ‘Known to be human carcinogens’ (NTP, 2011).

Significantly increased mortality due to lung cancer were reported in workers in cadmium processing plants, cadmium recovery plants and those who worked in the nickel-cadmium battery production industry (IARC, 2012). An increased risk of lung cancer was identified in workers with long-term employment in high cadmium-exposure jobs.

A few cases of cancer of the prostate, pancreas and kidney have also been reported following exposure to cadmium (either from occupational exposure or by contamination).

In some of these cases, workers may have been exposed to other chemicals, including arsenic and nickel. Both IARC and the US NTP concluded that the increase in lung cancers could not be solely due to coexposure to other chemicals (NTP, 2011; IARC, 2012). However, the Agency for Toxic Substances and Disease Registry (ATSDR) disputed that the interpretation of these observations in humans is complicated by co-exposure with other metals, and that there is a 'lack of significant relationship between cadmium exposure and duration' (ASTDR, 2012). These data suggest that there is limited evidence of cancer of the prostate, pancreas and kidney occurring from exposure to cadmium compounds in these studies.

Cadmium sulfide is classified as hazardous (Category 2 carcinogens) with the risk phrase 'May cause cancer' (T; R45) in HSIS (Safe Work Australia). Based on the available data, there is sufficient evidence from animal studies and observations in humans to warrant this classification applying to the compounds in this group, unless bioavailability by inhalation can be demonstrated to be very low.

## Reproductive and Developmental Toxicity

The analogue, cadmium sulfide, is classified as hazardous (Category 3 substance toxic to reproduction) with the risk phrases ‘Possible risk of impaired fertility’ (Xn; R62) and ‘Possible risk of harm to the unborn child’ (Xn; R63) in HSIS (Safe Work Australia). While there are no experimental data available for any specific chemical in this group, results from cadmium chloride (by oral exposure) and cadmium oxide (by inhalation exposure) indicate that reproductive effects (fertility and developmental effects) were detected at dose levels that also caused general toxicity and maternal toxicity.

***Reproductive toxicity***

In a study in male and female F344/N rats and male and female B6C3F1 mice, animals were exposed to cadmium oxide by inhalation at 0.025, 0.5, 0.1, 0.25 or 1 mg/m$^3$ for 13 weeks. Decreased spermatid counts and increased oestrous cycle lengths were reported in rats in the highest dose groups, as well as decreased body weight gain and increased mortality. No treatment-related histopathological changes of the reproductive organs were seen. In mice, there was no reproductive toxicity reported at any exposure level (NTP, 1995). A reproductive LOAEL of 1 mg/m$^3$ was reported for this study based on the effects observed in rats (NICNASa).

***Developmental toxicity***

In a developmental toxicity study in SD rats, animals were exposed to cadmium oxide by inhalation at 0.05, 0.5 or 2 mg/m$^3$ on gestation days (GD) 4–19. Exposure-related foetal skeletal variations (reduced ossification of the pelvis and the sternebrae) and reduced foetal weights (statistically significant in the highest dose group) were reported. However, significantly decreased maternal body weights and reduced absolute liver and kidney weights were also recorded at the highest dose, in addition to one mortality at GD 17. Signs of toxicity were observed in dams in all treatment groups. The effects included dyspnoea (difficult or laboured breathing) and hypoactivity (NTP, 1995). A maternal NOAEL of <0.05 mg/m$^3$ and a developmental NOAEL of 0.5 mg/m$^3$ were reported for this study (NICNASa).

In another study, Swiss mice were exposed to cadmium oxide by inhalation at 0.05, 0.5 or 2 mg/m$^3$ on GD 4–17. An increased frequency in reduced ossification of the sternebrae was reported in foetuses (statistically significant at the highest dose), while significantly reduced foetal weights were reported at ≥0.5 mg/m$^3$. Signs of toxicity, including dyspnoea and hypoactivity, were observed in dams from all treatment groups, in addition to significantly reduced maternal body weights and five mortalities (euthanised moribund) from the highest dose group (NTP, 1995). A maternal NOAEL of <0.05 mg/m$^3$ and a developmental NOAEL of 0.05 mg/m$^3$ were reported for this study (EU RAR, 2007). Placental and lactational transfer of cadmium to the offspring (see **Toxicokinetics**) are also considered to be adverse to development (NICNASa).

As it is established that absorbed cadmium can be transferred to the foetus, there is sufficient evidence to warrant this classification applying to the compounds in this group, unless bioavailability by oral and inhalation routes can be demonstrated to be very low.

# Risk Characterisation

## Critical Health Effects

The critical health effects, depending on bioavailability of cadmium from the specific form of the chemicals, for risk characterisation may include systemic long-term effects (carcinogenicity; reproductive toxicity; skeletal, respiratory and renal effects from oral and inhalation exposure). Depending on the bioavailability, the compounds in this group may also be harmful following acute oral exposure.

## Public Risk Characterisation

The compounds in this group are listed on Schedule 6 of the SUSMP under the chemical group 'cadmium and cadmium compounds' (SUSMP, 2013). For the majority of potential public exposure routes, this schedule entry is expected to be appropriate.

## Occupational Risk Characterisation

Given the critical health effects, the compounds in this group may pose an unreasonable risk to workers unless adequate control measures to minimise exposure to the chemicals are implemented. The chemicals should be appropriately classified and labelled to ensure that a person conducting a business or undertaking (PCBU) at a workplace (such as an employer) has adequate information to determine appropriate controls.

# NICNAS Recommendation

Current risk management measures are considered adequate to protect public and workers' health and safety, provided that all requirements are met under workplace health and safety and poisons legislation as adopted by the relevant state or territory.

The recommended risk management measures were based on a 'worst-case' scenario where the presence of bioavailable cadmium was considered to be similar to that from cadmium sulfide. However, if high temperature calcining and/or surface

treatment processess can be demonstrated to mitigate the risk associated with the use or manufacture of products containing the chemicals in this group, by reducing the cadmium bioavailability, then some or all of the recommended classifications may not be required.

## Regulatory Control

### Public Health

Products containing the chemicals should be labelled in accordance with state and territory legislation (SUSMP).

### Work Health and Safety

The compounds in this group are recommended for classification and labelling under the current Approved Criteria and adopted GHS as below. However, some or all of the classifications recommended below may not be required if substantial evidence can demonstrate that the occupational risks can be mitigated through industrial surface treatment processes.

This assessment does not consider classification of physical hazards and environmental hazards.

| Hazard | Approved Criteria (HSIS)[a] | GHS Classification (HCIS)[b] |
|---|---|---|
| Acute Toxicity | Harmful if swallowed (Xn; R22) | Harmful if swallowed - Cat. 4 (H302) |
| Repeat Dose Toxicity | Toxic: danger of serious damage to health by prolonged exposure through inhalation (T; R48/23) Toxic: Danger of serious damage to health by prolonged exposure if swallowed (T; R48/25) | Causes damage to organs through prolonged or repeated exposure - Cat. 1 (H372) |
| Genotoxicity | Muta. Cat 3 - Possible risk of irreversible effects (Xn; R68) | Suspected of causing genetic defects - Cat. 2 (H341) |
| Carcinogenicity | Carc. Cat 2 - May cause cancer (T; R45) | May cause cancer - Cat. 1B (H350) |
| Reproductive and Developmental Toxicity | Repro. Cat 3 - Possible risk of impaired fertility (Xn; R62) Repro. Cat 3 - Possible risk of harm to the unborn child (Xn; R63) | Suspected of damaging fertility or the unborn child - Cat. 2 (H361fd) |

[a] Approved Criteria for Classifying Hazardous Substances [NOHSC:1008(2004)].

[b] Globally Harmonized System of Classification and Labelling of Chemicals (GHS) United Nations, 2009. Third Edition.

[*] Existing Hazard Classification. No change recommended to this classification

## Advice for consumers

Products containing any of the compounds in this group should be used according to label instructions.

## Advice for industry

***Control measures***

Control measures to minimise the risk from exposure to the compounds in this group should be implemented in accordance with the hierarchy of controls. Approaches to minimise risk include substitution, isolation and engineering controls. Measures required to eliminate or minimise risk arising from storing, handling and using a hazardous chemical depend on the physical form and the manner in which the chemical is used. Examples of control measures which may minimise the risk include, but are not limited to:

- using closed systems or isolating operations;
- using local exhaust ventilation to prevent the chemical from entering the breathing zone of any worker;
- health monitoring for any worker who is at risk of exposure to the chemical if valid techniques are available to monitor the effect on the worker's health;
- air monitoring to ensure control measures in place are working effectively and continue to do so;
- minimising manual processes and work tasks through automating processes;
- work procedures that minimise splashes and spills;
- regularly cleaning equipment and work areas; and
- using protective equipment that is designed, constructed, and operated to ensure that the worker does not come into contact with the chemical.

Guidance on managing risks from hazardous chemicals are provided in the *Managing risks of hazardous chemicals in the workplace—Code of practice* available on the Safe Work Australia website.

Personal protective equipment should not solely be relied upon to control risk and should only be used when all other reasonably practicable control measures do not eliminate or sufficiently minimise risk. Guidance in selecting personal protective equipment can be obtained from Australian, Australian/New Zealand or other approved standards.

***Obligations under workplace health and safety legislation***

Information in this report should be taken into account to assist with meeting obligations under workplace health and safety legislation as adopted by the relevant state or territory. This includes, but is not limited to:

- ensuring that hazardous chemicals are correctly classified and labelled;
- ensuring that (material) safety data sheets ((m)SDS) containing accurate information about the hazards (relating to both health hazards and physicochemical (physical) hazards) of the chemical are prepared; and
- managing risks arising from storing, handling and using a hazardous chemical.

Your work health and safety regulator should be contacted for information on the work health and safety laws in your jurisdiction.

Information on how to prepare an (m)SDS and how to label containers of hazardous chemicals are provided in relevant codes of practice such as the *Preparation of safety data sheets for hazardous chemicals— Code of practice* and *Labelling of workplace hazardous chemicals—Code of practice*, respectively. These codes of practice are available from the Safe Work Australia website.

A review of the physical hazards of the chemicals has not been undertaken as part of this assessment.

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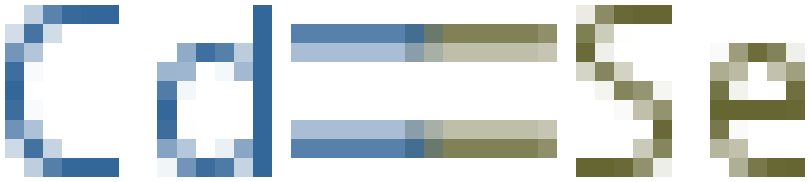
Last Update 18 September 2014

## Chemical Identities

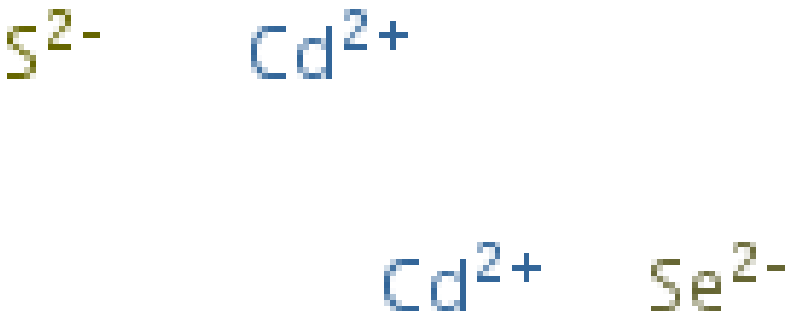
| | |
|---|---|
| Chemical Name in the Inventory and Synonyms | **Cadmium selenide (CdSe)** |
| CAS Number | 1306-24-7 |
| Structural Formula | |

| | |
|---|---|
| |  |
| Molecular Formula | CdSe |
| Molecular Weight | 191.37 |

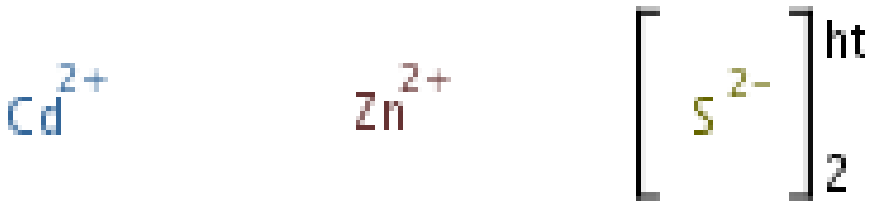
| | |
|---|---|
| Chemical Name in the Inventory and Synonyms | **Cadmium selenide sulfide, (Cd2SeS)**<br>dicadmium selenide sulfide<br>C.I. Pigment Red 108<br>C.I. 77202 |
| CAS Number | 12214-12-9 |
| Structural Formula |  |
| Molecular Formula | Cd.S.Se |
| Molecular Weight | 335.85 |

| | |
|---|---|
| Chemical Name in the Inventory and Synonyms | **C.I. Pigment Yellow 35**<br>C.I. 77205<br>cadmium zinc sulfide yellow |
| CAS Number | 8048-07-5 |
| Structural Formula | |

| | |
|---|---|
| | **No Structural Diagram Available** |
| Molecular Formula | Unspecified |
| Molecular Weight | Unspecified |

| | |
|---|---|
| Chemical Name in the Inventory and Synonyms | **Cadmium selenide sulfide, (CdSeS)**<br>Cadmium sulphoselenide<br>cadmium sulfide selenide (CdS0-1Se0-1) |
| CAS Number | 11112-63-3 |
| Structural Formula |  |
| Molecular Formula | CdSSe |
| Molecular Weight | 335.85 |

| | |
|---|---|
| Chemical Name in the Inventory and Synonyms | **Cadmium zinc sulfide, (CdZnS)**<br>C.I. 77205 |

| | |
|---|---|
| CAS Number | 12442-27-2 |
| Structural Formula |  |
| Molecular Formula | Cd.S.Zn |
| Molecular Weight | 241.93 |

| | |
|---|---|
| Chemical Name in the Inventory and Synonyms | **Cadmium selenide sulfide**<br>Cadmium sulfoselenide<br>cadmium sulfide selenide (CdS0-1Se0-1) |
| CAS Number | 12626-36-7 |
| Structural Formula |  |
| Molecular Formula | Cd.S.Se |

| | |
|---|---|
| Molecular Weight | 335.85 |

| | |
|---|---|
| Chemical Name in the Inventory and Synonyms | **C.I. Pigment Orange 20**<br>C.I. 77202<br>cadmium orange<br>cadmium sulfoselenide orange |
| CAS Number | 12656-57-4 |
| Structural Formula | **No Structural Diagram Available** |
| Molecular Formula | Unspecified |
| Molecular Weight | Unspecified |

| | |
|---|---|
| Chemical Name in the Inventory and Synonyms | **C.I. Pigment Red 108**<br>Cadmium red<br>C.I. 77202<br>cadmium sulfoselenide red |
| CAS Number | 58339-34-7 |
| Structural Formula | |

| | |
|---|---|
| | No Structural Diagram Available |
| Molecular Formula | Unspecified |
| Molecular Weight | Unspecified |

| | |
|---|---|
| Chemical Name in the Inventory and Synonyms | **Cadmium sulfide (CdS), solid solution with zinc sulfide, copper chloride doped**<br>Zinc cadmium sulfide, copper chloride doped |
| CAS Number | 68512-49-2 |
| Structural Formula | No Structural Diagram Available |
| Molecular Formula | Unspecified |
| Molecular Weight | Unspecified |

| | |
|---|---|
| Chemical Name in the Inventory and Synonyms | **Cadmium sulfide (CdS), solid solution with zinc sulfide, silver chloride doped**<br>Zinc cadmium sulfide, silver chloride doped |

| | |
|---|---|
| | |
| CAS Number | 68583-45-9 |
| Structural Formula | No Structural Diagram Available |
| Molecular Formula | Unspecified |
| Molecular Weight | Unspecified |

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