

ENVIRONMENTAL AND HEALTH ASPECTS^{BNL-61501} OF COPPER-INDIUM-DISELENIDE THIN-FILM PHOTOVOLTAIC MODULES

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Abstract

Copper-indium-diselenide (CIS) is a semiconductor compound that can be used to produce thin-film photovoltaic modules. There is on-going research being conducted by various federal agencies and private industries to demonstrate the commercial viability of this material. Because this is a new technology, and because scant information about the health and environmental hazards associated with the use of this material is available, studies have been initiated to characterize the environmental mobility and environmental toxicology of this compound. The objective of these studies is to identify the environmental and health hazards associated with the production, use, and disposal of CIS thin-film photovoltaic modules. The program includes both experimental and theoretical components and is funded by the Bundesministerium für Forschung und Technologie (BMFT). In parallel, the U.S. Department of Energy (DOE) and the National Institute of Environmental Health Sciences (NIEHS) funded an experimental program on biological systems. Theoretical studies are being undertaken to estimate material flows through the environment for a range of production options as well as use and disposal scenarios. The experimental programs characterize the physical, chemical e.g. leachability and biological parameters e.g. EC₅₀ in daphnia and algae, and feeding studies in rats.

Theoretical studies on the life cycle of solar modules

The complete lifecycle of almost all products includes:

- the starting material
- the manufacturing
- the installation, operation and use
- the recycling and disposal.

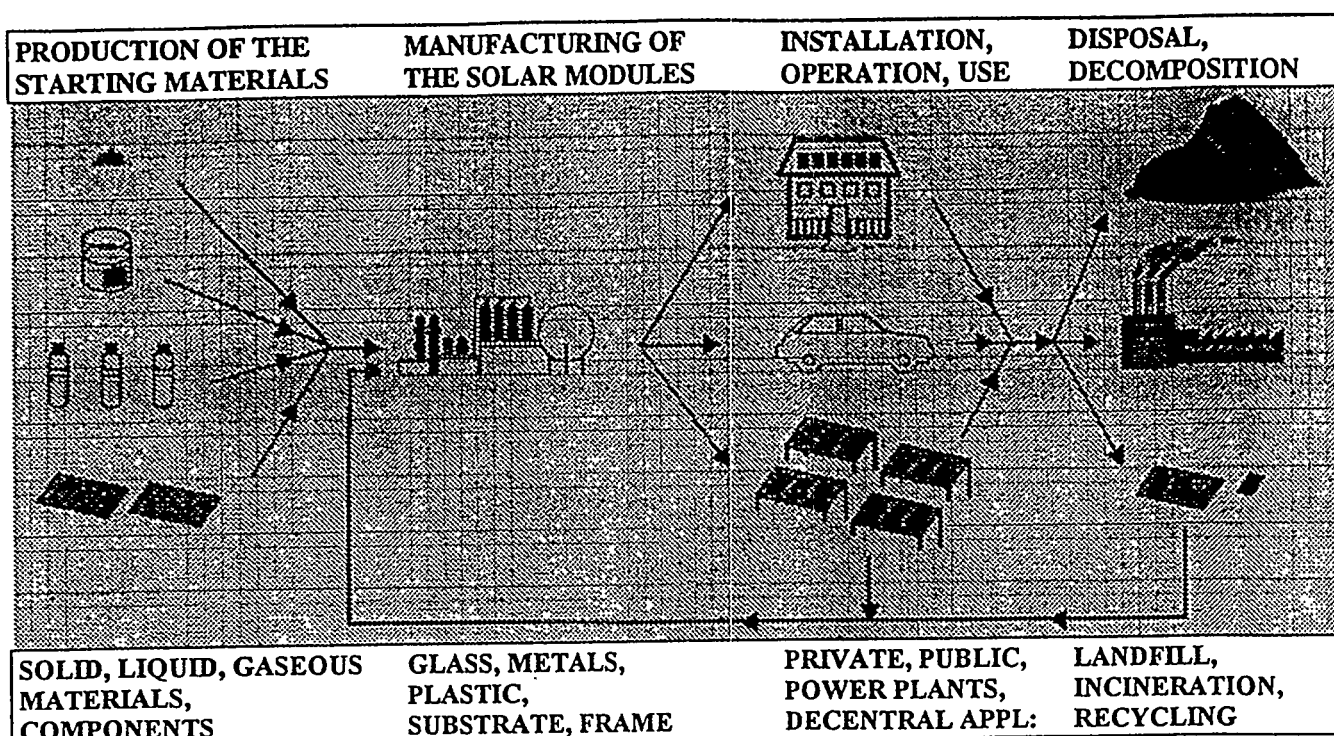
Today, nearly any type of marketing concept is based on a linear product path starting with the raw material and ending after usage with the disposal of the product. However, most product life cycles can be closed by a

recycling strategy based either on the product or material level.

In order to characterize all materials and material-paths into air, water and soil in the life cycle of our selected product for the thin-film modules we define the areas of investigations according to the following:

In the production of starting materials for the thin-film modules, solids, liquids, gaseous materials (elements and compounds) and prefabricated components must be considered. Solar module manufacturing uses these materials including the substrate, thin-films, laminates, cover glass, junction boxes, cables and frame materials. For the installation, operation or use we have restricted the photovoltaic (PV) modules to power application products like solar power plants or solar houses or to public accessible products like solar powered emergency call boxes on highways. Normal operation and accidents must be examined. Disposal including landfilling and incineration are issues to be investigated with their contribution of the material and material-flows of the products and byproducts into the environment e.g. drain-water, decomposition gas, slag or electro-filter dust and exhaust fume.

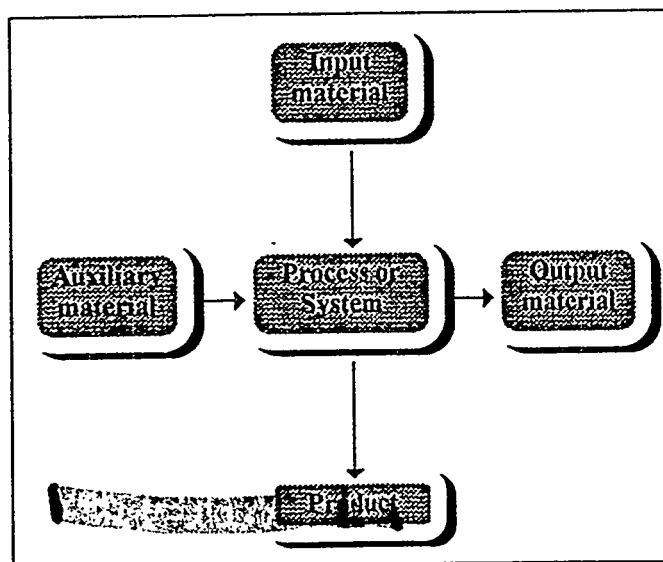
The entire lifecycle of a photovoltaic module shows outputs of rejected matter in every stage of the linear product line, e.g. of the incoming and outgoing materials at the specification control, of the final product after manufacturing or at the usage, when reduced power occurs. Inputs of reusable materials to the product line are possible at the refining processes of starting materials or somewhere at the module manufacturing. Inputs of systems, components or subsystems are fed back into the product line at manufacturing or before disposal (Fig. 1).



1. Lifecycle of a solar module

This investigation concentrates on the materials and paths of materials during the lifecycle of a solar module, but excludes all materials for solar module mounting systems, batteries, converters, and grid connections. It also excludes the energy consumption of module or material production processes.

The principal material flow of input, output and auxiliary substances in a single processing step is shown in Figure 2. Input materials are all materials partly or totally transformed into the product. Auxiliary materials are all materials taking part in the processing but not remaining in the product. Output materials are the rejected input materials or the rejected auxiliary materials (Steinberger, 1994).



2. Definition of input, output, auxiliary materials

Starting materials

The weight ratio of the element within the uppermost shell of the earth is called the total abundance. In order to identify the highest need for the conservation of resources, Table 1 compares the total material abundance, the annual production rate, and the minimum material consumption of important materials needed to produce 1 GW_e of solar modules. This roughly correlates to a 10 km² module area. Based on this analysis, it seems that indium (In) and selenium (Se) will be the bottleneck materials in future.

Material	Abundance	Production t/a	Consumption t/GW
copper	$1 \cdot 10^{-4}$	9,300,000	1100
indium	$1 \cdot 10^{-7}$	134	30
selenium	$8 \cdot 10^{-7}$	1,500	41
cadmium	$3 \cdot 10^{-5}$	18,000	3
molybdenum	$1 \cdot 10^{-5}$	117,000	76
soda lime glass	$1 \cdot 10^{-1}$	21,000,000	125,000

Table 1. Abundance, production and material consumption of important elements for thin-film module fabrication

Copper (Cu) mining is the most important source of selenium. As Se is found on the lower most right side of the periodic table, it shows a quasi-noble behavior and, therefore, is enriched like gold (Au) or silver (Ag) in the anode mud of the electrolytic refining method of Cu. Copper ores are found in many places in the world, but presently they are very diluted. Ores with a Cu content of more than 0.5 % are mineable. This means that 1,000 t of stones or rocks must be mined to be cracked and leached to produce 1 t of technically pure Cu.

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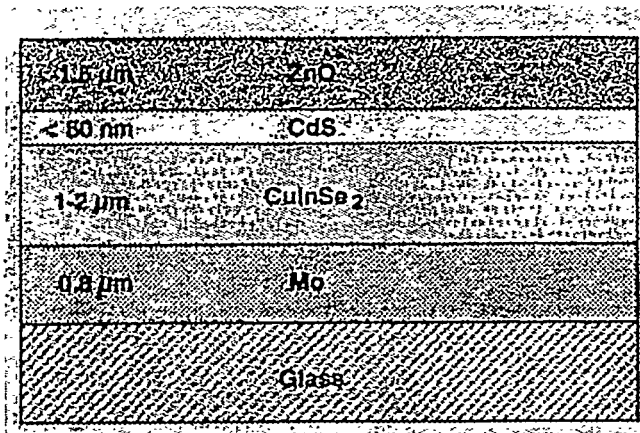
The Se production which is associated with the Cu production follows the mining rates of copper ores. About 10^6 t of stones must be moved for one ton of Se.

Zinc (Zn) production is the main source of In; about 7 million t are produced every year. Like Cu, about 10^6 t of stones must be processed for each ton of In produced.

Since In is noble and, in addition, shows a low melting point, but a high boiling point, it can be extracted from Zn by distilling. Electrolysis of In-rich Zn is done, too, in order to get technically pure In.

Manufacturing

The cell structure of a CIS-cell can be seen in Figure 3. Various thin-films are deposited on a glass substrate and covered by the front glass. In the homogeneous layers mechanical or laser structuring techniques form monolithically integrated parallel cells. The whole set of photoactive devices is called a module. For a CIS module the total material input of the critical element Cd is calculated for a 1 m^2 module area and a $1 \mu\text{m}$ layer thickness. CIS consumes roughly $1 \text{ g/m}^2/\mu\text{m}$ Cd for the cadmium-sulfide (CdS) layer formation as the total input material. In comparison CdTe uses 10 to $550 \text{ g/m}^2/\mu\text{m}$ Cd for the CdTe and CdS layer formation depending on the deposition technique.



3. Cross section of a typical CIS solar cell

Installation, operation, use

In the literature there is no reference to accidents or incidents during storage, but a few to transporting. Problems are known in the installation phase due to the malfunction of the electrical insulation, of the mechanical structure or the cabling along with broken glasses (van der Weiden 1991, Schaffrin 1991, Chianese 1991).

Breaks in cables, modules destroyed by snow storms, bubbles between the laminated glasses caused by temperature rises, mechanical impact on modules and stone throwing onto the modules are some of the problems externally created and reported in the literature during use and operation of silicon modules. Penetrating water in an aggressive environment near the sea or salt from highways

in wintertime and elevated temperatures have created short-circuits and corrosion. Sparks of thunder storms have destroyed many modules and entire systems in Germany, Greece and Italy. Electric short-circuits have been generated by servicing personal during installation or maintenance. In some cases melting of the cover glasses as a consequence of the high temperature in and around the sparks are reported. O'Riordan (O'Riordan 1991) has investigated the system in Ireland on the Fota Islands. Table 2 shows the different effects on the modules.

Reason for the problems	Numbers	% Ratio
Broken front glasses	22	28
Oxidation of front contacts	16	20
Color change of the substrate	15	19
Penetration of water	11	14
Broken substrate glasses	10	13
Broken ends	4	5
Laminate	1	1
In total for 2,772 modules	79	100

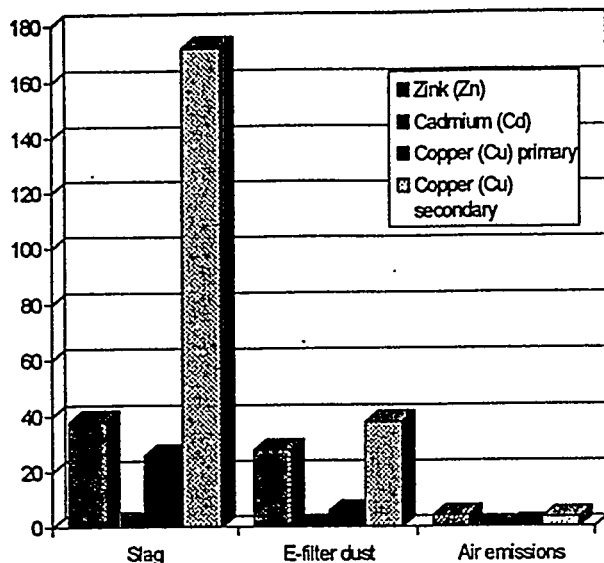
Table 2. Effects and problems of silicon solar modules on the Fota Islands in Ireland

Disposal

Different options for waste disposal are under discussion in Europe. Waste incineration is gaining more political interest and was indirectly implemented by the new legislative initiative in 1993 in Germany defining the "technical regulations for municipal waste". These new regulations do not allow wastes to be disposed at a regular landfill (Class 1 or 2) when metallic elements in an eluate or organic compounds in the ash of incinerated materials of a typical product exceed given limits. The content of metallic elements in the eluate has to be proved following the German leaching test DEV S4. The remaining organic compounds in the ash also have to be verified according to the German ashing standard tests. Since modern products mostly contain plastic materials, their ashes exceed the 3 % or 5% organic limits for Class 1 or Class 2 landfill deposition, respectively. Therefore they fail the municipal landfill regulations and have to be pretreated by waste incineration.

Slag and filter dust of a municipal waste incineration facility have to be tested in the same way (for metals and organics) before disposing in landfills. In case they exceed the limits for Class 1 or 2 landfills, they must be disposed in landfills for hazardous materials.

On the basis of an one year averaged distribution of input and output materials for a German municipal waste incineration facility (Nottrodt, 1975), we have estimated the total released material in slag, filter dust and pure gas dust assuming a 1 kW module input of CIS-technology, see Figure 4.



4. Output material distribution of a 1 kW CIS-module input into a municipal waste incineration facility in Germany

These estimations again take into consideration the materials both from the thin-film layers on the substrate (primary) and the frame materials (secondary). The main contribution in the case of CIS is Cu in the slag of around 200 g in total, of 43 g in filter dust and 4 g in the released gas dust. Cadmium is represented in slag as 1.5 g, as 0.5 g in the filter dust, and around 0.05 g in the released gas dust.

Recycling

Preexperiments on commercially available CdTe-modules for recycling have been carried out using liquid nitrogen, sand blasting techniques and HCl etching. Liquid nitrogen has peeled off large areas of thin-film layers. The remaining residues on the surface of the glass substrate were then etched back by HCl, which left a clean transparent glass substrate showing small reflecting zones along the removed structuring lines. Sand blasting with two different sand particle sizes (50 mm glassbeads and 70 mm corundum) seems also possible for recycling, if the working speed can be controlled in the correct processing window to avoid surface cracks or holes of the glass substrate. Similar studies are being prepared for CIS modules.

Experimental work

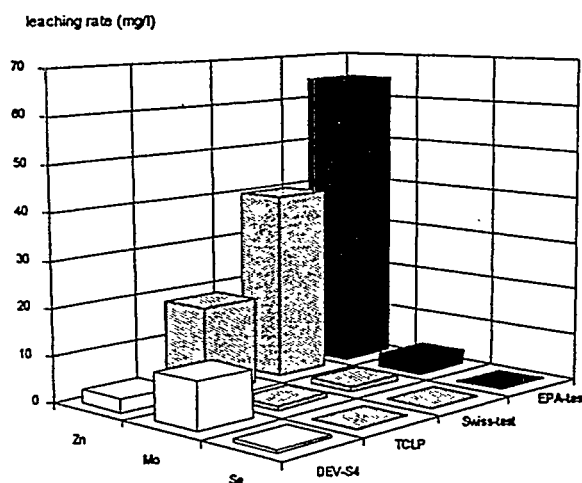
Leaching tests

The physico-chemical part of our work started with elution tests. A part of these tests is performed outdoors. CIS modules and fragments are exposed to natural weather conditions. The eluates are sampled at convenient time periods and analyzed. These experiments began in 1992 and will be finished in 1994 (Thumm, 1994).

The situation in landfills is simulated by nationally and internationally approved elution tests. Four different

methods are used, the German test Deutsches Einheits Verfahren (DEV S4), the U.S. Environmental Protection Agency Toxicity Characterization Leachate test (EPA TCLP), the Swiss test and an elution test developed at the University of Wisconsin for EPA. They have in common that the samples are rotated end over-end for 24 hours with an eluant.

Zn, molybdenum (Mo) and Se are the elements eluted in the highest amounts from fragmented CIS solar modules. In Fig. 5, a comparison is shown between the different tests and the concentrations found in the eluates. Zn is eluted in the highest amounts at low pH and high complexing agent content, whereas Mo and Se are eluted better at higher pH. They are supposed to elute as anionic species and this may explain their behavior.

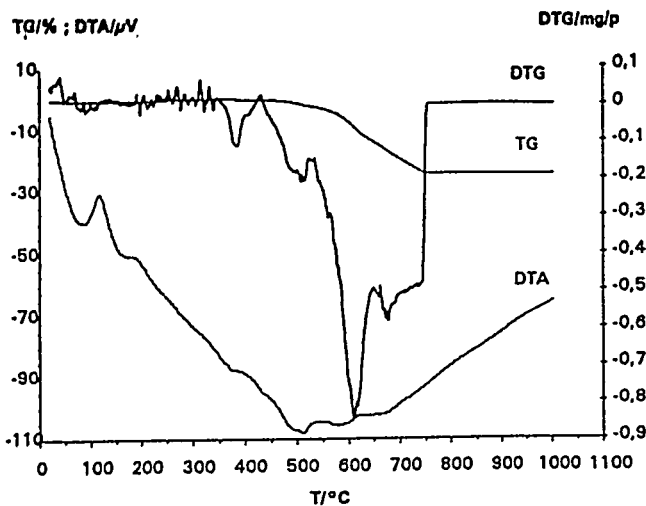


5. Element concentration in the eluate of DEV S4, TCLP, EPA and Swiss test

For waste disposal in a landfill Class 1 in Germany the element concentration in the eluate according to the DEV S4 test is limited for Zn to 2 mg/l (found 1.6 mg/l), not limited for Mo and Se, for Cu to 1 mg/l (found 10.5 µg/l), and for Cd to 50 µg/l (found 16 µg/l). In the U.S. the element concentrations are not regulated for waste disposal in landfills for Zn, Mo, but for Se and Cd to 1 mg/l (found 60 µg Se/l and 31 µg Cd/l) regarding to the TCLP test. Thus the tested modules pass both tests.

Heating tests

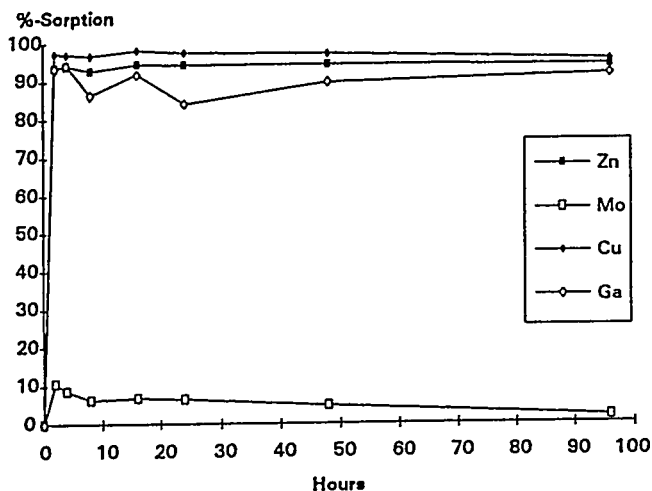
Figure 6 shows the results of a differential thermal analysis. Samples of pure CIS material were heated in air. Important information can be deduced from the thermogravimetry curve. For CIS, a weight loss of 27% is found starting at 300 °C. This corresponds to the replacement of the entire Se by oxygen (O) and the release of selenium dioxide (SeO₂).



6. Differential thermal gravimetry (DTG), thermal gravimetry (TG), differential thermal analysis (DTA) on pure CIS material in air

Sorption tests

In the sorption experiments with soils and clay minerals, usually a strong sorption is found for cationic species, whereas the sorption for anionic species like molybdate is rather faint. This is illustrated by Figure 7. For Se in its two possible anionic species, the situation becomes more difficult, because selenite is a strong adsorbent in contrast to selenate which usually is a weak one.



7. Sorption tests on lufa 2.1 soil for CIS material

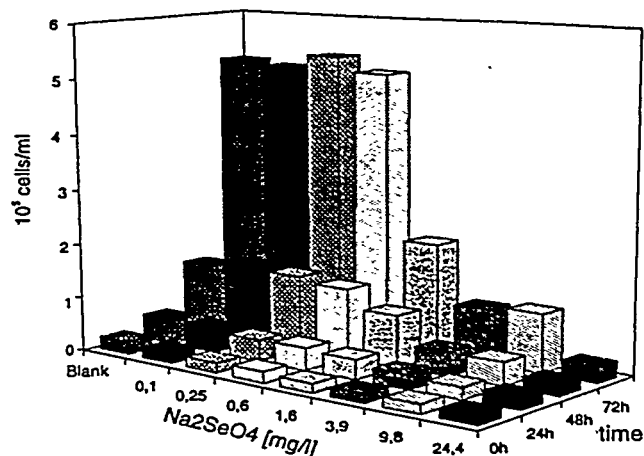
Toxicity tests on *Daphnia magna* and algae

In toxicity tests, the effects found were dependent on the speciation of the single elements tested. That means, the oxidation state as well as the counterions influence toxicity. This effect is demonstrated in the Table 3 for toxicity tests with *daphnia magna* (waterflea) for Se. The same effect can be observed in other toxicity tests. In further experiments, combinatory effects of compounds that may come into existence from solar cells have to be taken into account.

Test substance	EC ₅₀ (mg/l of element)	element
K ₂ Cr ₂ O ₇	0.2	Cr
Na ₂ SeO ₄	2.2	Se
Na ₂ SeO ₃	3.7	Se
ZnSO ₄	1.7	Zn
K ₂ TeO ₃	5.6	Te

Table 3. *Daphnia magna* - acute toxicity (24h-Test)

Figure 8 shows the result of an acute toxicity test with algae for sodium selenate. Selenium in its different speciations shows a non-classical behavior in some toxicity tests; at rather low concentrations, no toxic action can be detected, but a small stimulating effect can be observed.



8. Acute toxicity on algae

For further experimental work, it will be necessary to focus more on the speciation of the elements that are able to enter the environment, because the impact and the effect of these elements on compartments of the environment greatly depends on their speciation.

Rats study

To determine the toxicity of the thin-film materials of the PV modules, a short term toxicity study was undertaken using rats as the model species. First, a pilot study was performed to set doses for the main study. The main study evaluated a number of endpoints of systemic toxicity, as well as potential reproductive and developmental effects (Chapin, 1994).

Groups of mature male and female Sprague-Dawley rats were administered an aqueous suspension of CIS in 0.5% methylcellulose by gavage at levels of 0, 50, 100, and 250 mg/kg of body weight. Three groups of short term toxicity evaluations were conducted. Comprehensive examination of the male rats was made. Histopathology was performed of the liver, kidney, spleen, testis, right epididymis, and left caudal epididymis as well as clinical chemistries, hematology and sperm count and motility.

Males showed no difference in body weight and food consumption across all dosing levels. While a statistically

significant liver weight increase was seen at the top dose, the clinical chemistry measurements did not indicate any hepatic changes. The hematology data indicated a mild regenerative anemia with an isolated effect of monocytes (decrease in monocytes at the 100 and 250 dose level). No effects were seen on the male reproductive system. Neither organ structure nor fertility were altered by CIS exposure.

Females exposed during gestation (group 3) at doses of 100 and 250 mg/kg/day experienced a 15% lower weight gain than controls during treatment. Although no increase in post-natal deaths was seen, there was a slight dose-related decrease in pup number and a corresponding increase in pup weight. Pup post-partum maintenance and growth was not affected.

Continuously exposed females who received the highest dose level (250 mg/kg/day) of CIS gained half as much weight as the controls. However, these females also consumed less food than their respective controls. As no effect was seen on the number of total or live implants or corpora lutea during the study, we conclude that CIS produced no effect on ovulation, fertilization or embryo implantation.

Conclusion

The theoretical investigation showed few materials released as output materials in a linear product line along the life cycle of a CIS module. Cu, Zn, or Cd could be found at low concentrations in waste incineration facilities. Preexperiments on recycling with Cd Te modules seem to be transformable to CIS modules and are now taken into consideration.

Leaching experiments with CIS module pieces have reported materials to be leached with four different types of tests in the ppm range for Zn, Mo and Se. Differential thermal analysis on CIS-compound material showed a significant mass loss in the temperature range above 600 °C and the sorption in lufa 1.2 soil for Zn, Mo, Cu and Ga was around 90%.

Daphnia tests were treated with various chemical compounds. Acute toxic effects for chromium were observed stronger than for Se or Te. For algae the Se seems as an essential element in the organism in low concentration according to our experiments.

The initial rat studies are important because of the chemical specific information they provide. The limited exposure duration of this studies constrains our ability to extrapolate these data over longer times and lower doses. Nevertheless, these studies suggest that CIS has low acute toxicity.

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