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Inherent occupational health hazards in the production of solar grade silicon

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ABSTRACT

Solar energy has become one of the most developed renewable energy sources in recent years. As with any energy source or product, there are health risks associated with the manufacturing of solar cells. And even though the photovoltaic industry uses far lesser amounts of toxic and flammable substances than many other industries, the use of hazardous chemicals can present occupational and environmental hazards. One of the most important aspects in the selection of new processes lies in the protection of workers' health. Health risks can be reduced if a process is chosen properly and in preliminary phases. Since we have found that it is necessary to carry out an evaluation of the health risks to workers in the production of polycrystalline silicon for the manufacturing of photovoltaic cells, in this work we will use the Process Route Healthiness Index to quantify the health risk that each silicon production process represents (the higher the index, the higher the hazards). The polycrystalline silicon production processes evaluated with the healthiness index are: Siemens Process, Intensified Fluidized Bed Reactor Union Carbide Process, and Hybrid Process. Our results show that the Siemens Process is the healthiest process, but with the Process Route Healthiness Index values are closer to the Hybrid Process. Apart from this, a guide to the assessment of inherent occupational health hazards in Si_{SG} production processes was also developed, which provides results alike those to the PHRI methodology.

1. Introduction

In recent years, the energy industry has paid special attention to productivity improvement, to waste reduction and to quality control, all in the areas of research, development, and manufacturing. This is due not only to the consideration of cost reduction, but also to the awareness of sustainability increase in the manufacturing process (Cave and Edwards, 1997). Although it is known that the processes of obtaining non-renewable energy impacts the environment in various ways. The processes of non-renewable energy production by their nature turn out to be potentially dangerous for human and environmental health (Owusu and Asumadu-Sarkodie, 2016).

To achieve this, there are two approaches to make these processes healthier, safer and more environmentally friendly, called internal and external means (Hassim and Edwards, 2006). However, the use of internal media, commonly known as an inherent approach, turns out to be better, since it is based on the fundamental properties of the process, on the nature of the chemicals required by the process and on the conditions of the process (Adu et al., 2008; Warnasooriya and Gunasekera, 2017). If, in the inherent approach a chemical does not exist, it does not represent any danger. Therefore, the inherent approach requires less protection systems, which will make them more manageable (Edwards and Lawrence, 1993).

However, there are not many studies that assess the principles of inherent occupational health hazards in energy production processes from renewable sources. It is believed that renewable energy and its obtaining process turn out to be harmless. In spite of this, each one of the parameters or principles of health hazards has to be evaluated in order to compare and to decide which process is more appropriate under this approach.

Inside the renewable energies, the energy from the sun is the most abundant. It is estimated that it could cover around 35% of the total energy that the United States will require by 2050 (Fthenakis et al., 2009). Presently, research on the potential of solar energy continues on the economic, social and technical aspects, as well as being compared to the potential of fossil fuels. Contrary to fossil

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Nomenclature

AP	Penalties for activities
C	Carbon
CH	Chemical hazards
CP	Penalties for conditions
EI99	Eco-indicator 99
H_2	Hydrogen
$HCl_{(g)}$	Hydrogen chloride
HHI	Health Hazard Index
ICPHI	Inherent Chemical and Process Hazard Index
IR	Individual risk
IROSF	Inherent Risk of Occupational Health of Silicon Production Facilities
MHI	Material Harm Index
OEL_{min}	Minimum Occupational Exposure Limit
PH	Physical Hazards
ROI	Return on investment
$SiCl_4$	Silicon tetrachloride
SiH_2Cl_2	Dichlorosilane
SiH_4	Silane
$SiHCl_3$	Trichlorosilane
Si_{MG}	Metallurgical grade silicon
SIO_2	Silicon dioxide
Si_{SG}	Solar grade silicon
WC	Working conditions
WEC_{max}	Maximum Worker Exposure Concentration
WOPF	Work Organization and Psychosocial Factors

fuels, solar energy is based on cost per kilowatt and in recent years, the United States, China and countries in the European Union, have implemented initiatives to reduce the cost of solar energy per watt. In some cases, as in a project developed by *First Solarse*, it has managed to reduce the cost as far as one U.S. dollar per watt (United States Department of Energy, 2012).

Renewable sources have been steadily pairing up to fossil fuels in economic value; and, despite the idea that these are "clean resources", they also represent a continuous struggle with the environmental and health risks that they themselves may cause. Solar industry is no exception. Nowadays, the massive production of solar panels has resulted in a problem that needs special attention due to the use of toxic compounds that are harmful for both humans and the environment.

Despite the aforementioned, there exist evidence that solar panel production is much safer for the environment and workers than fossil fuel energy production (Galland, 2012). However, this raises the question to the evaluation problem in health and environmental aspects in solar panel production. Even if the photovoltaic industry uses far fewer amounts of toxic and flammable substances than many other industries, the use of hazardous chemicals can represent occupational and environmental hazards. Nowadays, there are reports that consider health, environmental impact and industrial hygiene in the photovoltaic industry (Briggs and Owens, 1980; Taylor, 2010; Fthenakis and Moskowitz, 2000). These reports display discussions about aspects among the various technologies of photovoltaic cells production: monocrystalline and polycrystalline silicon cells, gallium arsenide cells, cadmium sulfide cells. However, none of these reports show in detail the health aspects that represent each of the processes for raw material production in the manufacture of cells.

There is a great array of materials for solar panel production, the leading technologies at a commercial level are silicon-based, whether it be monocrystalline or polycrystalline (Briggs and Owens, 1980). In 2010, silicon represented 88% in all the photovoltaic cells (Price et al., 2010). A key point in the manufacture of silicon based solar cells is the acquisition of raw material. The literature shows two industrial consolidated processes for the acquisition of silicon polycrystalline, the first one is the Siemens Process, which is the most widely used (Bye and Ceccaroli, 2014). The second one is the Fluidized Bed Reactor (FBR) from Union Carbide (Erickson and Wagner, 1952). Moreover, Ramírez-Márquez et al. (2018) proposed an improved FBR process, called Hybrid, which conceptually results in higher production of silicon polycrystalline, in addition to being suitable in economic, safety and environmental aspects (Ramírez-Márquez et al., 2019).

Even though in the work by Ramírez-Márquez et al. (2019) aspects such as economy, environmental impact and safety are addressed, it is important to make a detailed study of the evaluation of inherent occupational health hazards of the three processes; this, due to the nature of said processes, since these represent a real potential hazard to the operator's health, and they require the use of raw materials (in liquid, solid and gas state) with inherent toxicological properties which can represent a health risk (Warnasooriya and Gunasekera, 2017).

That is why a polycrystalline silicon production health risk evaluation must be a determining factor for selecting the best route. Although there is research that evaluates the inherent occupational health hazards issues in the early stages of design and help to choose the appropriate process route (Koller et al., 2000; Adu et al., 2008; Sugiyama, 2007).

In this work, we use the methodology of inherent occupational health hazards of Hassim and Edwards (2006) to assess the occupational health problems related in production of silicon polycrystalline in the three processes mentioned above. The Hassim and Edwards methodology (2006) is used because the technique takes into account both the hazard from the chemicals present, and the potential damage caused by the exposure of workers to chemicals. Assessing occupational health in all processes is of great importance since workers are exposed to dangerous chemical substances which can cause chronic diseases in the long run. With this in mind, it is necessary to identify hazardous substances and how to detect which parts of the processes cause the most damage in order to make improvements and prevent any type of incidents.

2. Methodology

The objective of this work is to estimate the risks for the occupational health in the three process designs for polycrystalline silicon production following the Hassim & Edwards methodology (Hassim and Edwards, 2006). This methodology was designed and developed to take into account the possible factors that could be a potential health risk in the workplace. To achieve this, certain factors that represent the Process Route Healthiness Index (PRHI) were estimated in a quantitative manner. The PRHI includes all the factors that contribute to the risks in the occupational health (Hassim and Edwards, 2006). A higher value of PRHI means that the process represents a greater risk in occupational health terms. Methodologies like the PRHI are very useful when comparing different processes to determine which process might represent the greatest damage to the health of workers and to identify possible solutions.

2.1. Case studies

The data obtained in the optimization performed by Ramírez-Márquez et al. (2019) have been considered; in it, the three processes for the silicon production under a multi-objective framework were optimized to account for safety, profitability and environmental impact. The indexes used were: Individual Risk

(IR), Return on Investment (ROI) and Eco-indicator 99 (EI99), respectively. The modeling of the processes was carried out in Aspen Plus V8.4. The optimization was carried out by a hybrid algorithm called Differential Evolution with Taboo List (DETL). The considered processes are briefly described in next sections.

2.1.1. Siemens process

The main raw materials for the first part of the Siemens process are quartz (SiO_2) and carbon (C). By introducing these compounds in an electric arc reactor, metallurgical grade silicon (Si_{MG}) is obtained. Then, with the use of Si_{MG}, H_2 and HCl that are fed into a fluidized bed reactor, the chlorosilanes ($SiCl_3$ and $SiCl_4$) are produced. The hydrogen (H_2) and hydrogen chloride (HCl) that are left are separated when chlorosilanes condense. Afterward, a distillation column is used to pull apart the chlorosilanes ($SiCl_3$ and $SiCl_4$) up to purities above 99.99%. The $SiCl_3$ is feed to the chemical vapor deposition reactor (CVD) of the Siemens Process for silicon deposition (See Fig. 1). In the vapor deposition reactor, products such as HCl, H_2, $SiCl_4$ are also obtained.

2.1.2. Intensified fbr union carbide process

In all three processes, the initial stage of carboreduction is the same. SiO_2 and C are required to reach Si_{MG}. First, the Si_{MG} is mixed with $SiCl_4$ and H_2 in a fluidized bed reactor. Secondly, with a separator (heat exchanger) the chlorosilanes are condensed to separate them from the remaining gases. And finally, the chlorosilanes (SiH_2Cl_2, $SiHCl_3$ and $SiCl_4$) are separated into two conventional distillation columns. From the first column, a mixture of the light key components (SiH_2Cl_2, $SiHCl_3$) is obtained, and the heavy key component ($SiCl_4$) is removed from the bottom. Also, from the second conventional column the SiH_2Cl_2 is separated in the dome and $SiHCl_3$ at the bottom. Subsequently, silane (SiH_4) must be obtained with the use of reactive distillation, through the disproportion of the trichlorosilane. The reactive distillation column produces a high purity silane over the dome of the column. Afterwards, the SiH_4 is fed to the chemical vapor deposition reactor to produce high purity silicon and hydrogen. Finally, the polysilicon is solidified while the gases, mainly H_2 and HCl, are recycled (See Fig. 2).

2.1.3. Hybrid process

The Si_{MG} is produced as in previous cases, through the carboreduction of SiO_2. After that, with the use of $SiCl_4$ (FRB case), the Si_{MG} is hydrogenated for the production of chlorosilanes, and a mixture of chlorosilanes with reaction gases is obtained. To separate the gases, the mixture is passed through a heat exchanger, and the chlorosilanes are condensed so that they may pass into several distillation columns. From the second column and all through the bottom, the trichlorosilane is removed, which is introduced into the Siemens vapor deposition reactor. Lastly, the HCl and H_2 are separated from the Si_{SG} (See Fig. 3).

For more information on the models used for the three processes, consult the work of Ramírez-Márquez et al. (2018).

2.2. Assessment method for occupational health aspect

To evaluate the inherent occupational health hazards, an approach that quantifies and provides an index about the health hazard for a given process is necessary. As mentioned above, the three evaluated processes related to inherent occupational health hazards are: the Siemens Process, the Intensified FBR Union Carbide Process, and the Hybrid Process. Specifically, the parameters of each process were taken from the work by Ramírez-Márquez et al. (2019), which carried out the optimization of the processes contemplating aspects such as safety, environmental impact, and the profitability of the three processes. The parameters resulting from each process can be observed in the work of Ramírez-Márquez et al. (2019).

This work aims to perform an analysis of inherent occupational health hazards on the results of multiobjective optimization to include another primordial aspect in determining the most convenient process. In this project, an index called the Process Route Healthiness Index (PRHI) is used, this describes the inherent occupational health hazard in the processes.

The PRHI for each process is calculated by the following relationship:

$$PRHI = ICPHI \times MHI \times HHI \times \frac{WEC_{max}}{OEL_{min}} \quad (1)$$

where, ICPHI stands for Inherent Chemical and Process Hazard Index and evaluates the operating conditions, the conditions of the process and the properties of the materials involved that are potentially harmful to health; MHI represents the Material Harm Index and takes into account the limits of exposure, as well as the possible damages and/or effects that each of the substances can cause, the penalization of the substances is according

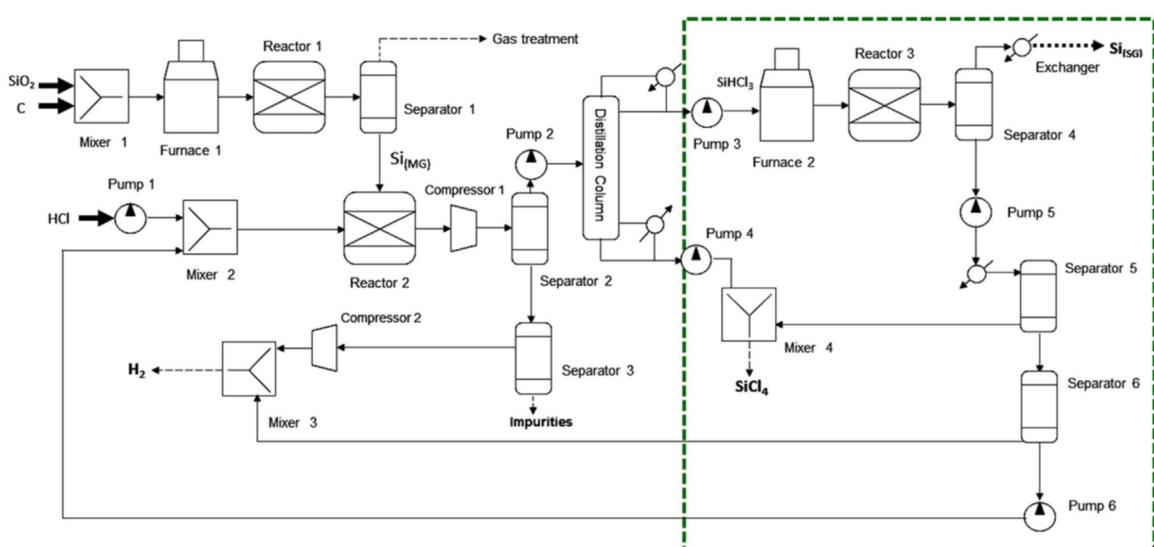

Fig. 1. Flowsheet Siemens Process.

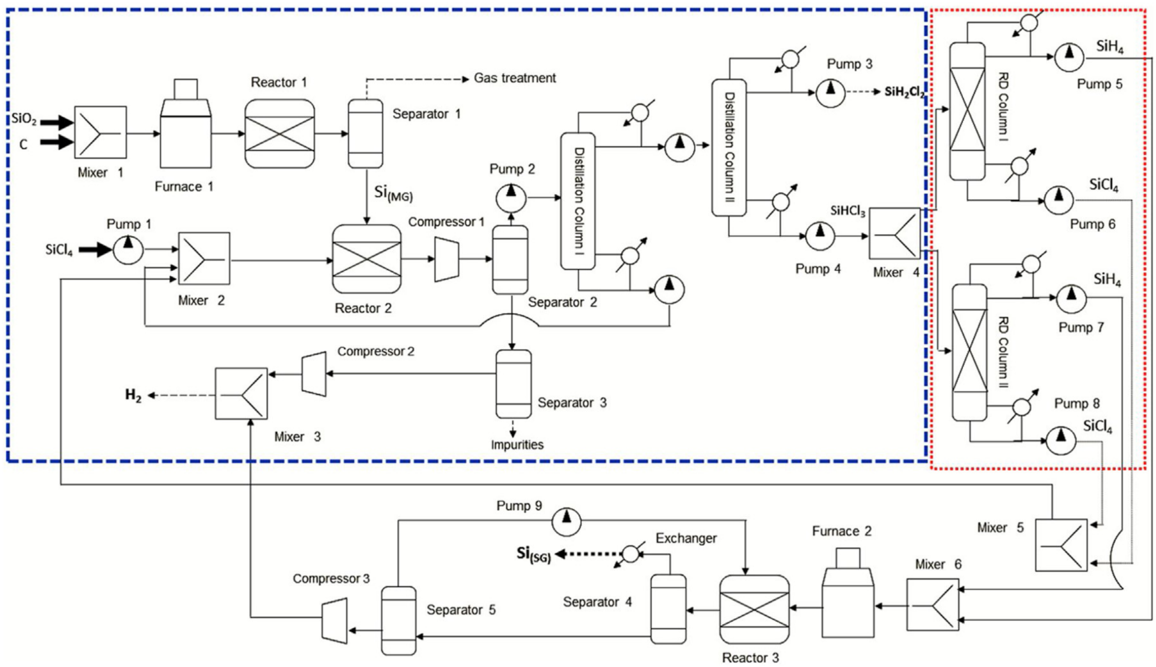

Fig. 2. Flowsheet of Intensified FBR Union Carbide Process.

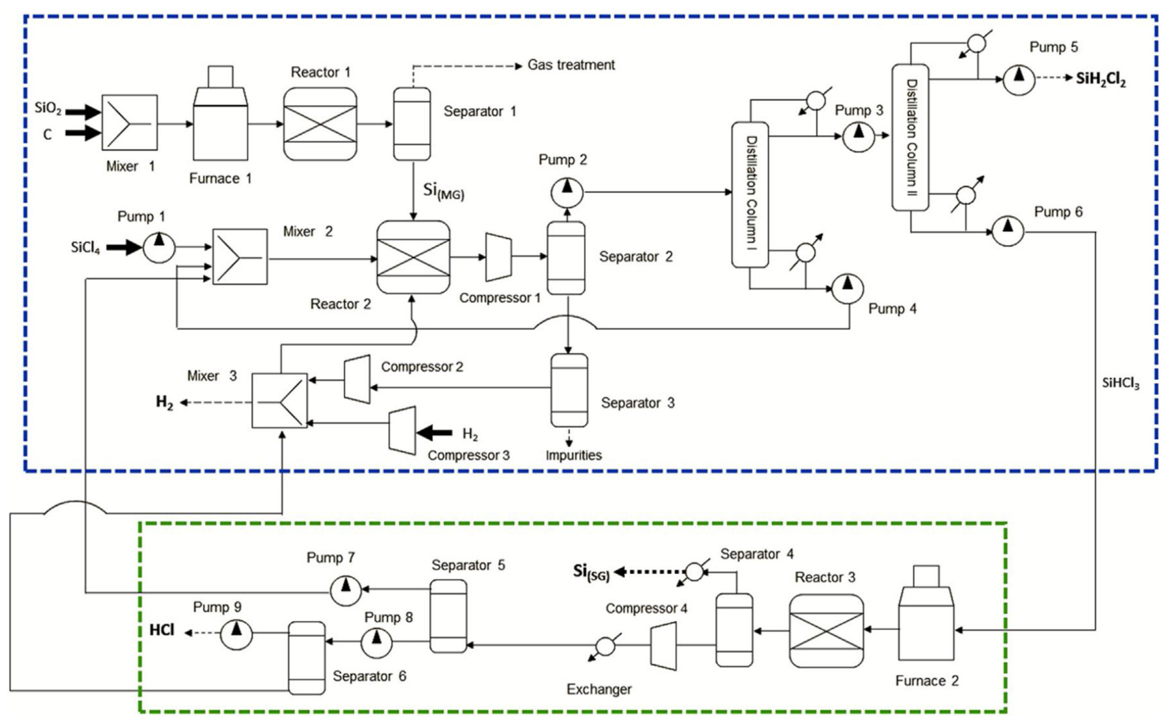

Fig. 3. Flowsheet Hybrid Process FBR Union Carbide with Siemens.

to the criteria of the NFPA; HHI symbolizes the Health Hazard Index and determines the ability of substances to cause occupational diseases, whether through irritation, sensitivity or cancer (this information is obtained from the OSHA database). WEC_{max} represents the maximum Worker Exposure Concentration and is the maximum concentration to which a worker is exposed to in the worst case and takes into account the quantity of substance that can be released to the work environment through emissions or small leaks and considers the relation between the estimated time of exposure of (6 h) and the average (8 h) of a normal working day; and lastly, OEL_{min} indicates the minimum Occupational Exposure Limit and represents the maximum concentration to which a worker will be exposed without any cause of damage.

The elements for calculating the PRHI are listed in Fig. 4.

Described above is an adequate methodology for the evaluation of occupational health in the silicon processes. Since, in the early process design stage some of information was not available. Hassim and Edwards (2006) presented a detailed methodology for calculating the PRHI.

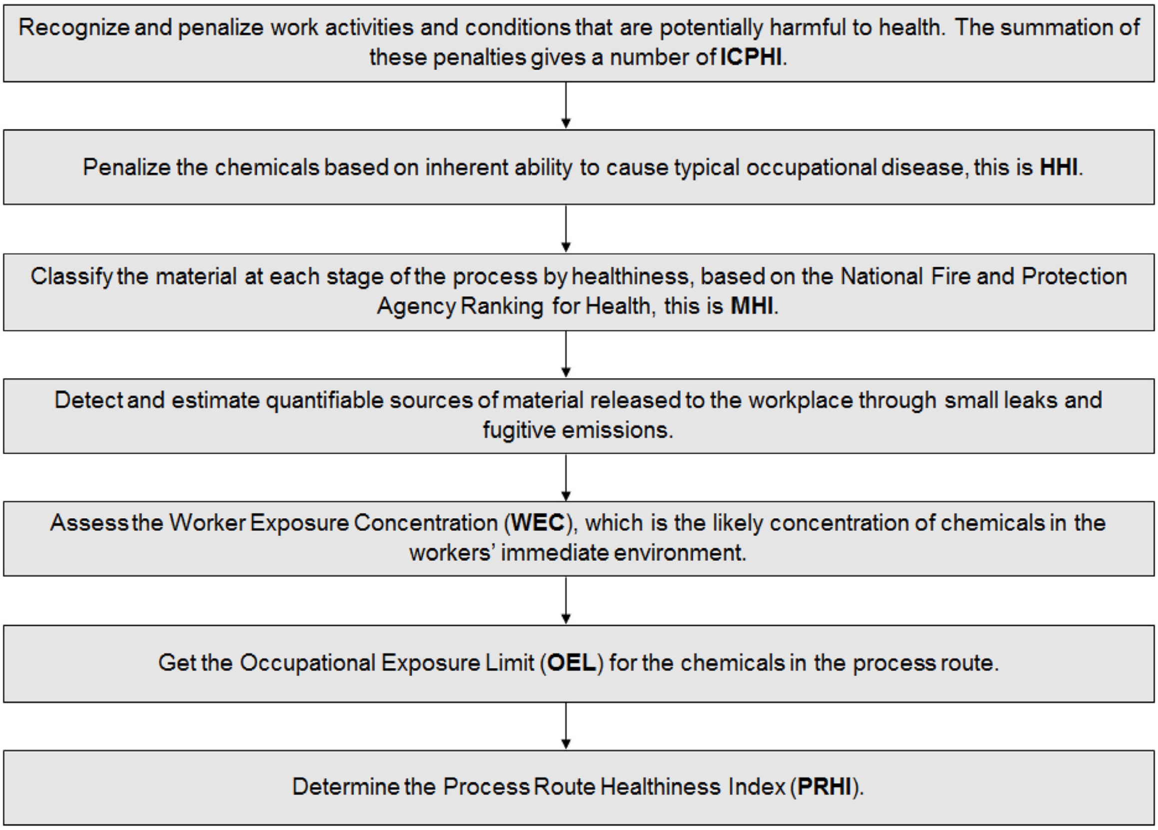

Fig. 4. Diagram for calculating the PRHI (Hassim and Edwards, 2006).

3. Results

This section presents the results of the evaluation of inherent occupational health hazards in the production of solar grade silicon, for three processes: Siemens, Intensified FBR Union Carbide and Hybrid. A summary of the healthiness index for each process is presented in Table 1, where all the results of the aspects considered by the PRHI are shown. The whole procedure of the evaluation of the PRHI for the FBR Union Carbide Process is presented in Appendix A.

The PRHI is then scaled to make it clearer and to facilitate the comparison of the results. The scaled healthiness index values are listed in Table 2. This is done by dividing the index by the highest index value calculated by the three silicon production process routes that are being compared. The highest value of PRHI is presented in the Intensified FBR Union Carbide Process.

It is important to break down each of the elements included in the evaluated PRHI for each of the solar grade silicon production routes. The quantification of the total penalties for activities (AP) in the Siemens and Hybrid processes are equal with a value of 42, leaving only 4 process sections to be evaluated, while in the Intensified FBR Union Process a process unit plus which raises the penalty for activities to 51 is required. The important value to highlight in the AP is the transport type of each section of the process. Carboreduction's highest value being a vibratory transport (similar in all three processes) which may be hazardous in the workplace. Because all work activities in the production process of solar grade silicon have a high exposure to noise pollution, safety is an important subject that must be addressed in order to prevent health problems among workers. In the total penalties for conditions and properties (CP), the points to be differentiated in the three processes are the operating conditions (Temperature, Pressure, etc.), as well as the changes in volume and the physical state of the components in each unit. The temperature in the carboreduction reactor can increase to more than 1999 °C in all three processes. A marked differentiation in the operating conditions can be found in the chlorosilane synthesis reactor and deposition reactors. In the case of the Siemens Process chlorosilane synthesis reactor, the temperature increases to more than 259 °C with a pressure of 4.93 atm, while in the other two processes, the temperature can increase to more than 500 °C and a pressure of 35.54 atm (See Appendix A and B). The above-mentioned makes a significant difference in the risks inherent in these items, however the quantitative difference marked in these conditions is somewhat rewarded by the changes in volume and the state of matter generated in the reactor.

The Health Risk Index (HHI) plays a very important role in the three processes, dealing with the capacity of the chemical products involved in each route of the processes which cause typical occupational diseases. The main exposure effects of each substance are shown in Appendix A. The difference in the HHI values for each evaluated process lies in the presence of different compounds and of its irrigation. The highest HHI value is recorded for the Intensified FBR Union Process due to the presence of SiH_4 and SiH_3Cl because of their high values of toxicity and damage it causes to the nervous system (See Appendix A). The Siemens process has the lowest HHI value since the hazard of the substances that are handled in this process are of low risk. The assessment of the material damage index (MHI) assigns values ranging from 1 to 4 to chemical products according to reactivity, flammability and its health risks. In this item and in all three processes, compounds such as Si_{SG}, C, SiO_2, and SiH_4 are given a value of 1 (indicating the least dangerous condition) for items such as exposure irritation. While compounds such as SiH_2Cl_2, $SiCl_4$, $SiHCl_3$, CO, SiH_3Cl, are given values of 3 and 4 (indicating the most dangerous condition) which may cause serious injuries and even death (See Appendix A). As a result from this, the Intensified FBR Union Process represents the

Table 1
Summary of Results.

	AP	CP	ICPHI = AP + CP	HHI	MHI	WEC_{MAX}	OEL_{min} (kg/m^3) 10^6	PRHI 10^{-14}
Siemens	42	30	72	29	15	2510	2.48	0.316141562
Intensified FBR Union	51	40	91	38.6	21	61279	4.98	9.085718795
Hybrid	42	30	72	33.3	19	4282	2.49	0.784304839

AP, Penalties for Activities; CP, Penalties for Conditions; ICPHI, Inherent Chemical and Process Hazard Index; HHI, Health Hazard Index; MHI, Material Harm Index; WECmax, Worker Exposure Concentration; OELmin, Minimum Occupational Exposure Limit.

Table 2
Scaled Healthiness Index.

	$PRHI_{SCALED}$ (Damage/kg Si)	$PRHI_{SCALED}$ (Damage)	Ranking
Siemens	0.03480	1.92275	1
Intensified FBR Union	1.00000	183.26040	3
Hybrid	0.08632	18.97388	2
1–Posses the best case.			

greatest danger in this area because of the existence of all these compounds.

The WEC_{MAX} values shown in Table 1 indicate the maximum concentration in each of the Si_{SG} production processes for different groups of workers including process operators, maintenance personnel, laboratory/instrument technicians and research and development scientists. The highest value of WEC_{MAX} is shown in the Intensified FBR Union Process of 61,279 (kg/m^3), and this is due to the high value of fugitive emissions from the process due to the nature of the process and the components present in each unit.

The OEL is a useful reference standard value that compares the concentrations of the chemicals to which workers are exposed. The Intensified FBR Union Process with the greatest amount of compounds, the highest volume and being the most dangerous contains the highest value with 4.98×10^{-6} (kg/m^3) almost twice as much as those in the Siemens Process. The PRHI value of each of the processes are shown in Table 1, with the Siemens Process being the one with the lowest inherent occupational health hazards and the Intensified FBR Union Process representing the highest value of inherent occupational health hazards.

The result analysis shows the many reasons that raise the PRHI in the Intensified FBR Union Carbide Process. To summarize, this is partly due to the Intensified FBR Union Carbide Process having the major number of reaction steps and the use of various compounds in the process. It has the highest penalty for activities and conditions, the highest HHI and MHI values and the uppermost OEL. The conversion of trichlorosilane to silane is necessary for the deposition of polycrystalline silicon. In the reaction of disproportionation of trichlorosilane to silane, intermediate products (SiH_2Cl_2 and SiH_3Cl) are generated. These compounds are harmful to health, with a high value (of 4, where 5 is the maximum value) in the category of limited exposure-death/major residual injury. This according to the NFPA health rating criteria.

A different important aspect is generated in the chemical vapor deposition reactor in the Intensified FBR Union Carbide Process. Both, the high operating pressure of chemical deposition reactor and the boiling point of silane in the reactor is less than $-112\,°C$, which results in a very high value of airborne material generated from flashing liquid. On the one hand, it can be determined that the Intensified FBR Union Carbide Process presents the highest potential hazard to human health in producing polycrystalline silicon (See Fig. 5).

On the other hand, the PRHI value calculated for the Siemens Process does not demonstrate much difference from the Hybrid Process. Nevertheless, the PRHI for the Siemens Process is low compared to the other two processes. This is a repercussion of the process conditions and the unit operations involved in the Siemens Process.

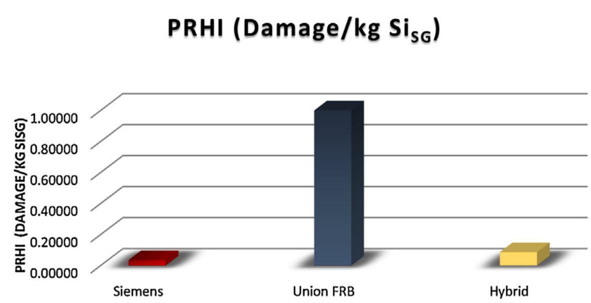

Fig. 5. Results of the PRHI (Damage/kg Si_{SG}).

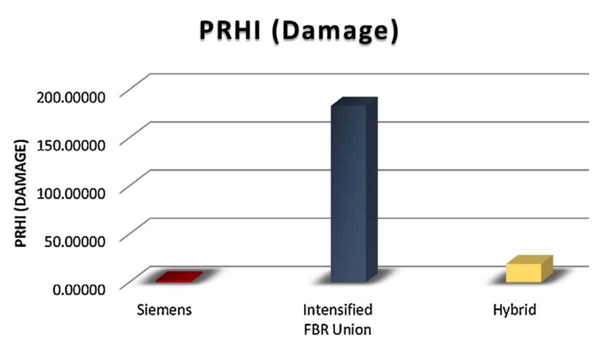

Fig. 6. Results of the PRHI (Damage).

The Siemens Process is similar to the Hybrid Process in terms of the involved compounds. The difference is the usage of $SiCl_4$ as a raw material in the Hybrid Process and HCl in the Siemens Process, which presents a similar health hazard to humans. An interesting fact can be seen in Fig. 6, where the difference between PRHI values of the Siemens Process and Hybrid Process tends to rise if the production of Si_{SG} is not considered.

The same three processes have been assessed by Ramírez-Márquez et al. (2019) in terms of their economic profitability (ROI), environmental impact (EI99) and inherent safety (IR). The Hybrid Process ranks as the second worse process in almost all aspects, however, as mentioned before, the difference between the Si_{SG} production for the Siemens Process and the Hybrid Process is four times higher, as Table 3 shows.

The comparison of the processes by these five aspects are tabulated in Table 4. Based on this comparison, the Intensified FBR Union Carbide is the route that should not be considered when looking for the best process for producing Si_{SG}. From the comparison shown in

Table 3
Results of the PRHI (Damage/kg Si), PRHI (Damage), ROI [%], Eco-99 [MP/y], IR [1/y] and Production of Si_{SG} [kg/h].

	$PRHI_{SCALED}$ (Damage/kg Si)	$PRHI_{SCALED}$ (Damage)	ROI [%]	Eco-99 [MP/y]	IR [1/y]	Production of Si_{SG} [kg/h]
Siemens	0.03480	1.92275	35.17123	0.53797	0.00019	55.2587
Intensified FBR Union	1.00000	183.26040	15.38502	0.95079	0.00180	183.2604
Hybrid	0.08632	18.97388	15.21748	3.37415	0.00071	219.8015

Table 4
Comparison of health, profitability, environmental impact, inherent safety and production of Si_{SG}.

	$PRHI_{SCALED}$ (Damage)	ROI [%]	Eco-99 [MP/y]	IR [1/y]	Production of Si_{SG} [kg/h]
Best Process	Siemens	Siemens	Siemens	Siemens	Hybrid
↓	Hybrid	Hybrid/ Intensified FBR Union	Intensified FBR Union	Hybrid	Intensified FBR Union
Worst Process	Intensified FBR Union	–	Hybrid	Intensified FBR Union	Siemens

Table 4, the Siemens Process is potentially the healthiest, most profitable, safest and most environmentally friendly, but also with the lowest production of Si_{SG}. For greater Si_{SG} production, the Hybrid Process is an appropriate option.

In the proposed process for the production of solar grade silicon, it is evident that the risks that an employee encounters in the workplace is a function of the existing risks, the exposure levels to those risks, and the operating conditions of each unit. Therefore, it is necessary to carry out the exposure assessment. The risk being, the core of all occupational health and industrial hygiene programs in all stages prior to the construction of a facility. In this work, a fundamental part of process design is the use of a systematic method to characterize the inherent occupational health hazards in the production of solar grade silicon. However, it should be noted that once a comprehensive and organized characterization of employee risk exposures has been detailed, resources from occupational health programs should be allocated more effectively to reduce the health risks of the employees. This should include a better approach to training programs, better execution of medical surveillance programs, the effective purchase and implementation of control measures, and valuable data for program evaluation (Moskowitz and Fthenakis, 1991). Assessment of inherent occupational health hazards in the production of solar grade silicon should be supported by elements of silicon industry occupational health program, and should include the following important program areas: education and training, hazard communication, exposure and compliance monitoring, medical surveillance, personal protective equipment, labor practice controls, administrative controls, engineering controls, handling of hazardous materials, etc. (Laberge et al., 2014).

It is important to mention the hazards related to occupational health resulting from the production process of solar grade silicon in a real situation. These usually differ in each production area and to the number of chemical compounds handled (summarized in Table 5) (Wald and Jones, 1987). Primary exposures in Si_{MG} production are crystalline SiO_2 and coke powder. The handling of refined Si_{MG} in the manufacture of $SiHCl_3$ is a potential source of exposure to silicon dust as Si_{MG} is grounded. The chlorosilane production lines are actually highly automated, but exposure to silicon dust, $SiCl_4$, and HCl may occur during maintenance or accidents. There is a risk of fire with hydrogen. The Si_{SG} process (Siemens and FBR Union) is highly automated. The most significant risks include bell-jar breakage, open reactors between runs, and reactor maintenance where amounts of H_2, $SiHCl_3$, and silicon dust can leak into the plant. Hydrogen and fire leaks, and exposures to solvents (trichloroethane during reactor cleaning) can also occur (Wald and Jones, 1987). When the results obtained with the PRHI methodology are compared to those from Table 5, proposed by Wald and Jones, 1987, it can be noticed that the dangers inherent in chemical compounds by solvents, flammable gases, particles, acids, and added to extreme operating conditions tend to have greater risks inherent in occupational health.

Developing the assessment of inherent occupational health hazards in Si_{SG} production processes in the preliminary design stages

Table 5
Chemical Hazards by Production Areas and physical hazards by production areas.

Production areas	Particulates	Metals	Solvents	Acids	Flammable gasses	Systemic and respiratory toxins	Electrical	RF
Polycrystalline silicon	X		X	X	X		X	X
Single cristal ingot	X	X		X		X	X	X

Table 6
Penalties for working conditions (WC).

Equipments	Range	Temperature	Range	Pressure	Range	Material State	Range	Volumen Change (%)
Reactors	Low	0	Low	0	Gas	0	Low (>25%)	1
	High (>300 °C)	1	High (>5 atm)	1	Liquid	1	Medium (25-32%)	2
					Granules	2	High (33-50%)	3
Crushers	Low	0	Low	0	Gas	0	Low (>25%)	1
	High (>100 °C)	1	High (>1 atm)	1	Liquid	1	Medium (25-32%)	2
					Granules	2	High (33-50%)	3
Convencional distillation columns	Low	0	Low	0	Gas	0	Low (>25%)	1
	High (>200 °C)	1	High (>5 atm)	1	Liquid	1	Medium (25-32%)	2
					Granules	2	High (33-50%)	3
Reactive distillation columns	Low	0	Low	0	Gas	0	Low (>25%)	1
	High (>150 °C)	1	High (>3 atm)	1	Liquid	1	Medium (25-32%)	2
					Granules	2	High (33-50%)	3

Table 7
Sum of Penalties for working conditions (WC) for the three production processes of Si_{SG}.

Process	WC
Siemens	15
Intensified FBR Union	19
Hybrid	16

will help select the appropriate process route and should be one of the major design choices. In the present work it has also been of great help to show a related evaluation strategy associated with the inherent dangers of occupational health in Si_{SG} production processes or similar processes which may represent a useful tool for future works.

The proposed occupational health risk assessment for Si_{SG} production processes is based on the fact that the process with the highest score represents the greatest risk to occupational health.

This quick guide to the assessment of inherent occupational health hazards in Si_{SG} production processes focuses on the most significant risks in the sector, especially:

3.1. Working conditions (WC)

Si_{SG} production processes include a broad range of activities and are performed in different work environments, such as reactors, crushers, conventional distillation columns and reactive distillation columns. The risks that workers may be exposed to can be subject to the different tasks they perform and to the location they work in. The WC index takes into account the working conditions for the Si_{SG} production facilities, and the work carried out by Hassim and Edwards (2006) and Warnasooriya and Gunasekera (2017). The subject of penalties in this area are shown in Table 6. The sum of penalties for working conditions (WC) for the three production processes of SiSG, can be seen in Table 7.

3.2. Chemical hazards (CH)

Si_{SG} workers' exposure to chemicals depends on the type of products used as well as of the characteristics of the working environment where they are used and to the conditions of use. Workers may be exposed to a number of different chemicals: dust, soot and dirt residuals, complexing agents, and acids (hydrochloric acid), quartz, minerals and other inorganic substances (trace metals). These chemicals are not only contained in the mining products that they use.

Over-dosage, the mixture of different products or the incorrect use of some products may create unexpected chemical reactions and release hazardous substances. Some of these chemicals have irritant properties at low concentrations and are corrosive at high concentrations (bases or acids). When over-sprayed, are used without the adequate ventilation or are sprayed onto hot surfaces, certain chemicals can cause breathing problems. During the evaluation of the chemical risks that workers are exposed to, everything from the chemical substances contained in dirt, dust, soot particles, as well as the characteristics of the environment, the work process and the chemical components of the products used in each process must be taken into account. Subject to the chemical substances used, different diseases can arise, such as eye irritation, mucous membrane irritation, skin dermatitis, respiratory disorders, asthma and cancer. The chemicals contained in some cleaning agents may also be flammable or explosive. The CH index takes into account the compounds used and generated in the Si_{SG} production companies, and the list of the principal effects of exposure to each substance proposed by the Occupational Safety and Health Administration (OSHA) (Occupational Safety and Health Administration, 2020).The subject of penalties in this part are shown in the Table 8. The sum of penalties for Chemical Hazards (CH) for the three production processes of SiSG, can be seen in Table 9.

Table 9
Sum of Penalties for Chemical Hazards (CH) for the three production processes of Si_{SG}.

Process	CH
Siemens	29
Intensified FBR Union	38.6
Hybrid	33.3

3.3. Physical hazards (PH)

pH encountered in Si_{SG} production work include: falls from ladders, elevated platforms, moving or rotating machinery parts (not only from the work equipment used but also from the environment where the work is performed). The Si_{SG} production work is rather physically demanding for the musculoskeletal and cardiorespiratory systems. The posture of the Si_{SG} production workers tends to be strenuous as he/she may often find him/herself in difficult positions due to the poor ergonomic characteristics of the industrial equipment or because the work environment (confined places). Workers perform on a daily basis a high number of repetitive activities which sometimes require the application of high forces. The hazards related to the poor ergonomics of work equipment, are greatly related to the particular tool used and also to whether it is adapted to the features and specific needs of the worker taking into account their anthropometry, physical strength, etc. This blend of factors, puts them at high risk of developing musculoskeletal illnesses. An adequate work equipment and training are essential. The Si_{SG} production companies should consult workers in the purchase of equipment designed specifically to the needs of each worker. The pH index takes into account the environment of the Si_{SG} production facilities, and the list of the principal effects of the environment proposed by Fthenakis (2018).The subject of penalties in this part are shown in the Table 10. The data for the evaluation of this item in the Si_{SG} production facility were extracted from the work of Ramírez-Márquez, (2019) The sum of penalties for Physical Hazards (PH) for the three production processes of SiSG, can be seen in Table 11.

Table 8
Penalties for Chemical Hazards (CH) for all the compounds used and generated in Si_{SG} production facilities.

	Si	H_2	$SiCl_4$	$SiHCl_3$	SiH_2Cl_2	C	CO	SiH_4	SiH_3Cl	SiO_2
Chronic (cumulative) toxicity- long term	–	–	–	–	–	–	–	–	4.5	–
Acute toxicity	–	–	–	–	–	–	–	4.3	–	–
Nervous system disturbances-nervous system	–	–	–	–	–	–	–	–	3.5	–
Respiratory effects other than irritation (asthma)	–	–	–	3	–	–	–	–	–	–
Respiratory effects	–	–	2.5	–	2.5	2.5	–	–	2.5	–
Irritation: eyes, nose, throat, skin	–	–	1.8	1.8	1.8	1.3	–	–	1.8	1.5
Asphyxiants, anoxiants	–	–	–	–	–	–	1	–	1	–
Explosive, flammable, safety	–	–	–	–	–	–	–	–	0.8	–
Generally low risk health effects-nuisance particulates, vapours or gases	0.5	–	–	–	–	–	–	–	–	–

Table 10
Penalties for Physical Hazards (PH).

Equipments	Range	Height (m)	Range	Use of elevated platforms and ladders	Range	Moving or rotating machinery parts	Range	Confined places
Reactors	Low (0 –1 m)	1	Yes	0	Yes	0	Yes	0
	Medium 1.1-3 m)	2	No	1	No	1	No	1
	High (>3 m)	3						
Crushers	Low (0 –1 m)	1	Yes	0	Yes	0	Yes	0
	Medium 1.1-3 m)	2	No	1	No	1	No	1
	High (>3 m)	3						
Convencional distillation columns	Low (0 –1 m)	1	Yes	0	Yes	0	Yes	0
	Medium 1.1-5 m)	2	No	1	No	1	No	1
	High (>5 m)	3						
Reactive distillation columns	Low (0 –1 m)	1	Yes	0	Yes	0	Yes	0
	Medium 1.1-5 m)	2	No	1	No	1	No	1
	High (>5 m)	3						

Table 11
Sum of Penalties for Physical Hazards (PH) for the three production processes of Si_{SG}.

Process	PH
Siemens	18
Intensified FBR Union	23
Hybrid	20

Table 13
Sum of Work Organization and Psychosocial Factors (WOPF) for the three production processes of Si_{SG}.

Process	WOPF
Siemens	3
Intensified FBR Union	3
Hybrid	3

3.4. Work organization and psychosocial factors (WOPF)

The PV industry and more precisely the solar grade silicon industry are under constant pressure to deliver more flexible and inexpensive products. In consequence they often opt for a work organization that reflects the demands for flexibility, sometimes at the detriment of the workers' health and well-being. In terms of working hours, Si_{SG} production facilities mostly performed 24 h working days. However, this may lead to adverse effects for Si_{SG} facility workers, such as working at unsociable hours, social isolation, disruption of work-life balance, fatigue, higher risk of being victim of violence, or higher exposure to dangerous substances.

The fact that Si_{SG} facility workers are often in a precarious employment situation also contributes to work-life conflicts. The workload of Si_{SG} workers is high due to work intensification and high pace of work, deriving from the demands for an increasing flexibility and productivity from employers and chief. The work subjects are sometimes repetitive, monotonous and strenuous and cleaners have in general little control over the work organization and their job. In addition, they sometimes have to adapt rapidly to unplanned situations, additional demands from the company. Decreasing the workload, enriching the job content, or developing more team based jobs can be beneficial to the improvement and the wellbeing of workers. The WOPF index takes into account the employment situation of the Si_{SG} production facilities, and the list of the principal effects of the employment situation is proposed by Kuhn et al. (2018).The subject of penalties in this part is shown in the Table 12. The sum of Work Organization and Psychosocial Factors (WOPF) for the three production processes of SiSG. can be seen in Table 13.

The total of the sum of these four items will give the inherent risk of occupational health in the Si_{SG} production companies (Table 14).

$$IROSF = WC + CH + PH + WOPF \tag{2}$$

Table 14
The Inherent Risk of Occupational Health of Silicon production Facilities.

Process	IROSF
Siemens	65
Intensified FBR Union	83.6
Hybrid	72.3

Perceptibly, the results shown by the quick guide to assessment of inherent occupational health hazards in Si_{SG} production processes compared to the PRHI methodology follow the same trend since many of the resources used for the quick guide come from the PRHI methodology. However, other aspects have been added, such as the physical risks inherent in the facilities and psychological factors that a worker experiences in the completion of the evaluation. In both evaluation scenarios, the Siemens Process represents the one with the lowest occupational health risk. On the other hand, the Intensified FBR Union Process represents the worst occupational health risk in both cases. The quick guide to the assessment of inherent occupational health hazards in Si_{SG} production processes can be a worthy evaluation tool in case of similar scenarios.

4. Conclusions

The PRHI has been tested on three processes for Si_{SG} production, in accordance to the case study results, type of compounds, and the several operating conditions that play a key role in determining the level of inherent occupational health hazards. The compound boiling points and the equipment operating conditions (Temperature and Pressure) are two parameters that disrupt the value of the index. Moreover, the number of reactions involved in the processes also have a huge impact on the PRHI values. The index assessed in the three processes for polycrystalline silicon production proves that it is possible to attempt a quantification of inherent occupational health hazards in the initial stages of process design.

Table 12
Penalties for Work Organization and Psychosocial Factors (WOPF).

	Range	Salary	Range	Work hours	Range	Work environment
Process	Low (>10 minimum salary)	1	Low (1-8 h)	1	Bad	1
	Medium (2-10 minimum salary)	2	Medium (8-9 h)	2	Good	0
	High (minimum salary)	3	High (>9 h)	3		

According to the presented comparison of the different processes, the Siemens Process is hypothetically the healthiest, most profitable, safest and most environmentally friendly. That is, the process that best follows the concept of inherent occupational health hazards, but it is also the least productive. For superior Si_{SG} production, the Hybrid Process is the best suitable option. A quick guide to assessment of inherent occupational health hazards in Si_{SG} production processes was also developed, which could be a good evaluation tool of inherent occupational health hazards in case of similar scenarios.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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References

Adu, I.K., Sugiyama, H., Fischer, U., Hungerbühler, K., 2008. Comparison of methods for assessing environmental, health and safety (EHS) hazards in early phases of chemical process design. Process Saf. Environ. 86 (2), 77–93, http://dx.doi.org/10.1016/j.psep.2007.10.005.

Briggs, T.M., Owens, T.W., 1980. Industrial hygiene characterization of the photovoltaic solar cell industry (No. DHEW (NIOSH)-80-112). National Inst. For occupational safety and health, Cincinnati, OH (USA). Div. Of Surveillance. Hazard Evaluation and Field Studies, OSTI ID: 5265468.

Bye, G., Ceccaroli, B., 2014. Solar grade silicon: technology status and industrial trends. Sol. Energy Mater. Sol. Cell. 130, 634–646, http://dx.doi.org/10.1016/j.solmat.2014.06.019.

Cave, S.R., Edwards, D.W., 1997. Chemical process route selection based on assessment of inherent environmental hazard. Comput. Chem. Eng. 21, S965–S970, http://dx.doi.org/10.1016/S0098-1354(97)87627-2.

Edwards, D.W., Lawrence, D., 1993. Assessing the inherent safety of chemical process routes: is there a relation between plant costs and inherent safety? Process Saf. Environ. 71 (B4), 252–258.

Erickson, C. E., & Wagner, G. H., 1952. U.S. Patent No. 2,595,620. Washington, DC: U.S. Patent and Trademark Office.

Fthenakis, V.M., Moskowitz, P.D., 2000. Photovoltaics: environmental, health and safety issues and perspectives. Prog Photovoltaics: research and applications 8 (1), 27–38, http://dx.doi.org/10.1002/(SICI)1099-159X(200001/02)8:1<27::AID-PIP296>3.0.CO;2-8.

Fthenakis, V.M., 2018. Overview of potential hazards. In: McEvoy's Handbook of Photovoltaics. Academic Press, pp. 1195–1212, http://dx.doi.org/10.1016/B978-0-12-809921-6.00035-5.

Fthenakis, V., Mason, J.E., Zweibel, K., 2009. The technical, geographical, and economic feasibility for solar energy to supply the energy needs of the US. Energy Policy 37 (2), 387–399, http://dx.doi.org/10.1016/j.enpol.2008.08.011.

Galland, A., 2012. Best practices in photovoltaics manufacturing. 2012 38th IEEE Photovoltaic Specialists Conference, 001639–001642, http://dx.doi.org/10.1109/PVSC.2012.6317910.

Hassim, M.H., Edwards, D.W., 2006. Development of a methodology for assessing inherent occupational health hazards. Process Saf. Environ. 84 (5), 378–390, http://dx.doi.org/10.1205/psep.04412.

Koller, G., Fischer, U., Hungerbühler, K., 2000. Assessing safety health, and environmental impact early during process development. Ind. Eng. Chem. Res. 39 (4), 960–972, http://dx.doi.org/10.1021/ie990669i.

Kuhn, S., Milasi, S., Yoon, S., 2018. World Employment Social Outlook: Trends 2018. Geneva, ILO http://hdl.voced.edu.au/10707/448589.

Laberge, M., MacEachen, E., Calvet, B., 2014. Why are occupational health and safety training approaches not effective? Understanding young worker learning processes using an ergonomic lens. Saf. Sci. 68, 250–257, http://dx.doi.org/10.1016/j.ssci.2014.04.012.

Moskowitz, P.D., Fthenakis, V.M., 1991. Environmental, health and safety issues associated with the manufacture and use of II–VI photovoltaic devices. Sol. Cells 30 (1-4), 89–99, http://dx.doi.org/10.1016/0379-6787(91)90041-M.

Occupational Safety and Health Administration, Washington, DC 20210. Recovered from 2020. U.S. Department of Labor. http://www.OSHA.gov.

Owusu, P.A., Asumadu-Sarkodie, S., 2016. A review of renewable energy sources, sustainability issues and climate change mitigation. Cogent Eng. 3 (1), 1167990, http://dx.doi.org/10.1080/23311916.2016.1167990.

Price, S., Margolis, R., Barbose, G., Bartlett, J., Cory, K., Couture, T., Hemmeline, C., 2010. 2008 Solar Technologies Market Report (No. LBNL-3490E). Lawrence Berkeley National Lab. LBNL), Berkeley, CA (United States) https://www.nrel.gov/docs/fy10osti/46025.pdf.

Ramírez-Márquez, C., Contreras-Zarazua, G., Martín, M., Segovia-Hernández, J.G., 2019. Safety, economic and environmental optimization applied to three processes for the production of solar grade silicon. ACS Sustain. Chem. Eng., http://dx.doi.org/10.1021/acssuschemeng.8b06375.

Ramírez-Márquez, C., Otero, M.V., Vázquez-Castillo, J.A., Martín, M., Segovia-Hernández, J.G., 2018. Process design and intensification for the production of solar grade silicon. J. Clean. Prod. 170, 1579–1593, http://dx.doi.org/10.1016/j.jclepro.2017.09.126.

Sugiyama, H., 2007. Decision-making framework for chemical process design including different stages of environmental, health and safety (EHS) assessment. ETH Zurich., http://dx.doi.org/10.3929/ethz-a-005398654.

Taylor, D.A., 2010. Occupational Health: on the Job With Solar PV., http://dx.doi.org/10.1289/ehp.118-a19.

United States Department of Energy, "SunShot Initiative", 2012. http://www1.eere.energy.gov/solar/sunshot/. Additional savings could be realized by addressing the costs of permitting solar installations, last modified February 9.

Wald, P.H., Jones, J.R., 1987. Semiconductor manufacturing: an introduction to processes and hazards. Am. J. Ind. Med. 11 (2), 203–221, http://dx.doi.org/10.1002/ajim.4700110209.

Warnasooriya, S., Gunasekera, M.Y., 2017. Assessing inherent environmental, health and safety hazards in chemical process route selection. Process Saf. Environ. 105, 224–236, https://doi.org/10.