High purity composite briquette for direct UMG-Si production in arc furnaces

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Abstract

In the race towards photovoltaic (PV) cells having a specific investment cost inferior to 1 W_{p} , the current production cost (30\$/kg) of downgraded electronic Si (6N to 8N after chemical refining) would reach an unacceptably high cost portion of 20 %. The development of a low cost specific metallurgical route for the production of Solar Grade (SoG) Si at 15\$/kg is therefore gaining a strong interest. The processes that can be used combine several steps, like segregations and plasma torch or slagging followed by leaching, as the removal of B and P is tedious. A concentration below 1 ppm for both elements is targeted to get an acceptable efficiency level of the photovoltaic cells

In the Metallurgical Grade Si (MG-Si), the B and P contents are in average above 30 ppm as the carbon reduction materials used in the arc furnace are either rich in B (coal) or in P (charcoal). A decrease of both impurities by a factor 3 in the metallurgical Si i.e. the direct production of Upgraded Metallurgical Si (UMG-Si) would significantly improve the efficiency level of the resulting PV cells or decrease massively the costs of purification by shortening the number of process steps.

A composite briquette fulfilling the purity targets was developed. The composite contains several carbon materials with different levels of reactivities and quartz sand. The raw materials aspects, the paste and briquette preparation, as well as the final carbonization step are commented. The finished briquettes are free of volatiles and are mechanically and thermally very stable, thus ensuring stable arc furnace charges with minimum losses of dust and SiO gas. Semi-industrial trials including the downstream purification steps for the production of SoG-Si grade Si are contemplated.

From metallurgical Si to photovoltaic cells

The reduction of quartz raw materials with carbon materials in arc furnaces delivers MG-Si with purity close to 99 % (2N). Most of the Si is used as alloying elements¹ in metals having the same level of purity. The purity requirement for Electronic Grade Si (EG-Si) is far away (9N) from that of MG-Si. As long as the demand of Si for PV cells was much lower than the one of EG-Si, down-graded (6N to 8N) electronic metal was used. For low power off-grid panels the high costs of EG-Si was not an issue. The situation is changing with the fast increase of the solar branch producing electricity at a larger scale. The production of low cost specific SoG-Si is needed to meet the competitive target of 1\$/W_p for industrial electricity generation.

The chemical Siemens process, involving energy intensive deposition of hyper pure polysilicon feedstock from chlorosilanes, is complex and requires a huge investment (100'000\$/t). The production costs reach 30\$/kg while the one of the incoming MG-Si is just above 1\$/kg! The FBR silane process require less investment and energy but the costs still reach 25 \$/kg. A specific metallurgical route producing SoG-Si guaranteeing a high cell efficiency at a cost below 15\$/kg is badly needed².

The efficiency of PV cells is among other things strongly influenced by the P and B contents of the Si^4 . The figure 1 shows that it reaches a maximum plateau for concentration below 0.1 ppm and that the use of UMG-Si would significantly deteriorate the efficiency to an unacceptable low level. In the range of 1 ppm (SoG-Si) halving both impurities results in a gain above 4 % rel. for the cell efficiency. The same savings percentage is reached for the investment costs. As they are by far the larger contributor to the electricity production costs a high purity SoG-Si material is badly needed and the easiest way to obtain it is by using a high purity UMG-Si feedstock.

Where are P and B impurities in the MG-Si coming from? Beside the 2.5 tons of quartzite containing some ppm of P the arc furnace process requires about 1 ton of several carbon reduction and electrode materials. Some are based on wood others on coal, and eventually others on by-products of petroleum or metallurgical coke (tar) process. Up to six C containing materials can therefore be used namely, woodchips, charcoal, coal, petcoke and anthracite based paste with graphite core electrodes.

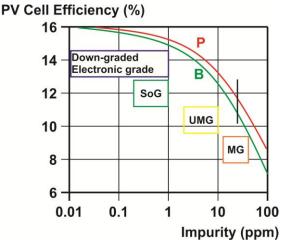


Figure 1: B and P impact on the PV cell efficiency

The	eoretical Mass	Balance	9	[SiO,<150mm	LOW ASH COAL	WOOD	CHAR COAL	CHAR	GREEN COKE
• 2	SiO ₂ + 2,14t SiO ₂ + 0,8				min					+	
	ctical Mass Ba to five Carbon		ants !	>3	0mm	, 	ł	4	RIPPEI	RCAR	
IN	Coal	0.3	t/tSi	~		1000					
	Wood chips	2.0	t/tSi								
	Charcoal	0.6	t/tSi		12	Z 1		L.			
	Char	0.3	t/tSi		min		mm	mini		mm	m
	SiO ₂	2.5	t/tSi		SCRAF	'	COLLI	ECTIO	N SCA	LE	
00	T Silicon	1	t			-/-	14				
	Silica	0.2	t/tSi					RAW MA	TERIAL	s	
	CO2	4	t/tSi	12W		un M	N TU	1t Si		11111	7

Figure 2: MG-Si production flow sheet and mass balance

Generally spoken, the wood and wood based charcoal are rich in P while the coal based products, like non-coking coal and char, are rich in B.

The figure 2 shows the theoretical and practical mass balance when a carbon charge is chosen with focus on equal contamination level of P and B. The efficiency of the process reaches today figures in the high eighties percents and about 0.2 t of micro silica are still generated, microsilica containing some volatile phosphorus components but no Boron species. This is due to the much lower melting points of the P components. The level of P loss from the carbon reduction materials reaches 90% .From the quartzite, melting only in the lower hot part of the furnace, the percentage loss is unfortunately lower (down to 50%). More than 90 % of B present in any raw materials is found in the metal^{2,5}.

The metallurgical route of purification during cooling of liquid Si involves segregation of impurities by directional solidification⁶. This works very well with most of the metals for which the coefficients of segregation (the ratio of concentration in solid versus the one in liquid) reach values close to 1/100'000 but is not very efficient for P (3/10) and for B (8/10). Multiple segregation steps are therefore needed for lowering their concentration below 10 ppm to obtain an upgraded metallurgical Si (UMG-Si). It is evident that a reduction of these two elements below the threshold of 10 ppm in the MG-Si would dramatically decrease the costs of purification for obtaining the SoG-Si.

For this purpose petroleum based coke material would be ideal from a purity point of view, but the amount of such reduction material in the charge is limited to some percent only, due to the lack of reactivity to SiO gas⁷ or to liquid SiO₂ for the formation of intermediate SiC prior its transformation to Si (see the simplified model inspired from Schei and Halvorsen⁸ in Figure 3). An excess of low reactivity carbon leads to poor efficiency and high energy consumption as well as to furnace operation difficulties.

However higher percentage of such low reactivity carbon have been used successfully, providing intimate contacts with finely distributed quartz favour the reaction rates⁹. This intimate contact means a production of composite briquettes with relatively fine quartzsand which is bounded with a suitable organic material, a concept already used in the eighties that was revisited and eventually reported below.

Past experiences and behavior on composite C/SiO₂ briquettes in furnaces

Briquettes industrially used in arc furnace

Smokeless briquettes as heating fuel have been developed in the sixties by DSM .The Eschweiler Bergwerksverein (EBV) constructed the Alsdorf (Germany) plant that was using a hot (500C) briquetting process with coking coal and breeze as raw material, completed by a subsequent post hardening step ¹⁰. More than 1.5mt of ANCIT briquettes were produced in 20 years till the plant has been shut-down after a severe fire, inherent to the risks associated with the high temperature process.

In the early eighties the plant was taken-over by Laborlux S.A. who developed with the same process a briquette containing about 50 % of quartzsand and 50 % of carbon in form of green petcoke bounded with coking coal for the metallurgical Si industry. In cooperation with IMC/AIMCOR this SANDANCIT briquettes were successfully used and

Kemanord reported a significant benefit in term of efficiency and electrical energy consumption (5 to 10%) in their DEMAG and ELKEM arc furnaces¹¹. The excess of C compared to SiO₂ in the composition of the briquettes (mol ratio of 5 instead of 2) meant that quartzite lumps were still added to the charge.

About one decade later, after preliminary pilot validations, AIMCOR has built a plant using a conventional continuous paste preparation unit (coal tar pitch as a binder) with the same raw materials basis and similar sand to carbon ratio. However the green briquettes were calcined at 550 C in a rotary kiln with a sand bed for oxidation protection so that a low volatile briquette material, named Silgro¹¹, could be offered to potential customers. The thermal and mechanical stability during the calcination was however insufficient in the full size kiln so that the yield in finished briquettes was too low and the high amount of scraps to be recycled was technically not anticipated in the plant design. After some industrial trials in the Si furnaces, where the disintegration of briquettes was resulting in high loss of fines, the plant was definitively shut down due to the poor economics compared to the classical loose charges.

Reaction mechanisms of conventional charges and of composite briquettes

With conventional lumps of quartzite the selection of the carbon blends was made according to the reactivity to SiO as high reactivity carbons trap the SiO in the outer zone of the furnace by transforming it into SiC, as shown in Figure 3. High reactivity being correlated with the porosity of the carbon material^{7,12} the preferred source was charcoal as during the carbonization of the wood more than 85 % of volatiles create a maximum of pores. Chars from non-coking coal (40 % of volatiles) have also an interesting high reactivity, but metallurgical cokes from coking coal and especially petroleum cokes are far less porous and therefore show low reactivity to SiO.

$$SiO_2 + 2C \rightarrow Si + 2CO$$
 (1)

• Overall assumed charge Mol ratio C/SiO₂ = 2

• **Outer zone**: SiO trapping with high reactive C

	SiO +	2	С	>	SiC	+	CO 7		(2)
•	Inter zone	:	SiO _{2 li}	quid	reacts	to SiC	C with I	ess reactive C	
	SiO _{2 liquid}	+	3 C	→	SiC	+	2 CO		(3)
•	Inner zone	e:	SiC re	acts	with	SiO _{2 lic}	_{luid} to g	ive Si and SiO	
	SiO _{2 liquid}	+	SiC	→	Si	+	SiO	+ CO	(4)
or	SiO _{2 liquid}	+	2 SiC	→	3 Si			+ 2 CO	(5)

Figure 3: Simplified reaction scheme for 100% SiO recovery

Therefore it is astonishing that briquettes with calcined coke materials from coking coal, green coke and coal tar pitch are operating well. From one side the faster melting of the fine quartz together with the intimate contact with the carbon components is quickly producing the needed SiC in the intermediate zone of the furnace. Another possible explanation is that the preferred reaction involving SiC and liquid SiO₂ in the inner hottest zone is the one producing no SiO but only Si, namely the reaction $#5^*$ as shown in the Figure 3.

It was also observed¹¹ that the reaction volume of the charge was much larger with briquettes, so that the velocity of the off-gas through the charge channels was reduced. Last but not least, the homogeneity of the charge was massively improved as the homogenization of the several raw materials having much different bulk densities and granulometries by simple stocking vehicle was, and remains, a tedious operation step.

Therefore less SiO reactive carbon components can do a correct job in term of efficiency and energy consumption. The ideal reaction sequence of briquette components for a 100 % yield is shown in Figure 4. The composite briquette still contains a relatively porous (C_p) and reactive carbon reacting with SiO but also an equivalent part of more dense carbon (C_d) that will react with SiO₂ later in the intermediate zone. The formed SiC will react with liquid SiO₂ from the molten lump quartzite in the lower inner part of the arc furnace.

Carbosil briquette process

In the past emphasis was given by the Si plants to the arc furnaces efficiency and to the energy consumption. The furnaces developments towards these goals were successful so that the interest for briquette projects has gradually fallen. A renaissance related to the expansion and potential of PV electrical energy is anticipated as briquettes of high purity can dramatically reduce the costs of the SoG-Si production. The strength and weakness of the raw materials and process used in the past were revisited and a composite briquette concept, delivering a product named *Carbosil*, was developed.

The strength of Sandancit briquettes were precisely their good mechanical and above all their high thermal stability in oxidizing atmospheres. The weaknesses of the hot briquetting process were not only its high fire risks but also the air and water pollution issues. Both aspects were solved with the Silgro process but the weaknesses, beside the poor yield during calcining, were the lack of thermal stability of the Silgro briquettes.

Emphasis was therefore given in producing a briquette that is maintaining its strength and integrity during the transformation process related to the formation of SiC from C with SiO oxidant gas or later with SiO₂. The knowledge gained in the manufacture of selective burning resistant anodes for the Al production was very helpful for this aspect.

The original idea of the patented concept¹³ is the cocarbonization process where the green briquettes are smoothly carbonized in a vertical retort¹⁴ together with one or more granular green carbons that will serve as carbonized raw materials for the production of the paste. The volatiles are burned close to the stoichiometry by controlled air injection and the resulting hot combustion gas are injected in the lower part of the retort, so that the heating of the incoming materials is maintained with or without additional fuel burners. The offgas is free from CO and tars after passing in a pyroscrubber system where air is injected. The flow sheet shown in Figure 5 shows the cycle process where eventually the finished briquettes are separated from the granular carbon by sieving.

In this continuous process an efficient high temperature screw preheater allows the usage of high softening point pitch with low volatile loss during the carbonization. High mixing power is achieved in a modern four flights kneader resistant to the sand abrasion. The paste is cooled in a cooler conditioner with controlled water injection and eventually shaped in briquettes in a high pressure roller press. These briquettes are stored after cooling and metered into the retort.

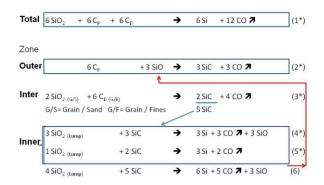


Figure 4: Reaction sequences with composite briquettes and quartzite lumps

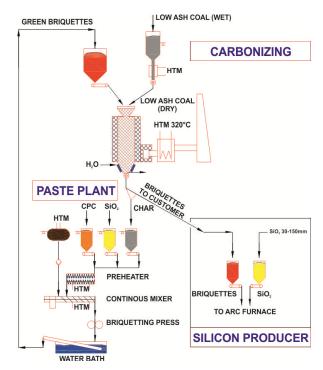


Figure 5: Carbosil plant flow sheet

The advantages of the retort carbonization are the smooth handling and devolatilization of the briquettes in a nonoxidizing atmosphere so that the briquette shape and integrity are guaranteed, and this with the lowest possible combustion loss. This last advantage is also valid for the green raw materials which, unlike in rotary kilns or travelling grates, are ideally carbonized from a yield point of view. The cost aspect is also important as low temperature static retorts are one order of magnitude cheaper than high temperature rotary kilns.

On a western world basis, the total investment of a 50'000 tpy *Carbosil* plant is around 20 m \$ with 1 manhour per ton wages and minimum costs of electricity and fuels. The raw materials are by far the main cost factor of the *Carbosil* production so that an optimum logistic is mandatory for minimizing transportation costs of quartzsand and briquettes to the end users.

Carbosil pilot composite briquettes

Pilot plant and testing tools (Figure 6)

The green granular carbons are carbonized preliminarily in a vertical pilot retort at a final temperature close to 750 C. The carbon dry aggregate is prepared by crushing, sieving in continuous pilot roller crushers and multi-decks sieving machine. The most important step, which is the fines preparation, request an air jet collision mill (zero iron contamination) equipped with an air classifier for controlling the fineness. The quartz sand is pre-dried at 120 C to guarantee precise proportioning and appropriate moisture less mixing conditions.

The batches of dry aggregate recipe are preheated before mixing in an intensive propeller mixer. The paste is cooled by water addition to the right temperature before the pressing of 20 cm^3 briquettes.

The green briquettes are co-carbonized with the corresponding amount of green materials that are later integrated in the carbonized form during the manufacture of briquettes. Obviously a smooth carbonization implies no agglomeration of the components related to too a high pitch content of the briquettes or to a coal having too a high Free Swelling Index, and requires a sufficient high bed permeability to the heating and volatiles gas. Therefore the right choice of the sizes and nature of the granular green materials is critical for avoiding clogging in the retort and appropriate heat treatment.

On the finished briquettes the apparent densities by a hydrostatic method, the load compression resistance in kg per briquette and the volatiles at 900 C are measured. The non SiO_2 ash is calculated and the Fe, Ca, Al, Ti and especially B and P contents are determined by ICP- OES with a detection limit below 1 ppm for these last two elements.

The most relevant test is the selective oxidation test derived from the well-known CO_2 reactivity test used in the Al industry for prebaked anodes (ISO 12988-1). The briquette is exposed at 960 C under CO_2 atmosphere for 7 hours. After cooling the partially reacted briquette is placed into a tumbler vessel, partially filled with small steel balls, in order to test the resistance to selective burning that is responsible of the partial disintegration of the briquettes. Higher ratio of carbon oxidation loss to the dust after tumbling means better resistance to disintegration of the composite briquette.



Figure 6: Pilot plant for the development of *Carbosil* composite briquettes

Physical characteristics of Carbosil briquettes

The table 1 shows the results of briquettes of similar dimensions and geometry with a level of C/SiO_2 weight ratio of 1 corresponding to a molar ratio of 5. The apparent density of the *Carbosil* composite briquette is the highest and its load strength reach unprecedented high levels thank efficient mixing of the optimized dry aggregate mainly.

The most encouraging data is the low selective burning and good integrity of the briquettes after the CO_2 reactivity test. The ratio loss to dust of the *Carbosil* briquettes reaches 4 times the Silgro value and is superior to the Ancit briquettes used with good success in the past.

These properties are practically independent from the choice of raw materials made on the purity criteria including the volatiles content that is remaining at a low 3 % level.

The purity of the *Carbosil* material is addressed below, where the contamination of the Si metals is estimated and compared to a typical charge of arc furnaces.

Impact of Carbosil on the Si metal purity

B and P from the charge components into the metal

Several papers^{2,5,15} addressed this topic as the volatility of the impurities present in the charge depends not only on the element considered but also from the raw materials in which the impurities are integrated. For instance the oxides of the alkali-metals like Na, K and Mg show a high volatility related to their low boiling point (less than 1000C) so that most of these oxides will be found in the microsilica and little (less than 10 %) will be found in the Si metal.

On the contrary as Boron oxydes show boiling point above 3000 C the majority (90%) of the incoming impurity will be transferred into the metal.

For P different distributions were observed as its volatility from the carbon reduction material is as expected high (10 %only in Si metal), but intermediate (50%) for the P impurities integrated in the large size quartzite lumps reacting only in the inner zone of the furnace.

Conventional charge situation for B and P in the MG-Si

For a comparison basis we can consider the production of MG-Si where raw materials purity and charge composition are selected in such a way to get an equal contamination of B and P in the metal. The Table 2 shows that due to the high content of B in coal or char and of P in charcoal a blend of carbon raw materials is mandatory.

Properties	Unit	ANCIT	SILGRO	Carbosil
Apparent Density	kg/dm ³	1.50	1.35	1.52
Load Strength	kg	120	80	140
Loss in CO ₂	%	14	18	13
Dust in CO ₂	%	11	54	9
Ratio Loss / Dust		1.2	0.3	1.4
Volatiles	%	4	6	3
Non SiO ₂ ash	%	3	2	0.2

 Table 1: Properties of Carbosil Briquettes compared to those of previous industrial products

		Dry basis			
Raw materials	Moisture %	Ash %	B ppm	P ppm	
Charcoal	5	2	5	140	
Coal	10	1.5	40	10	
Char	5	2	60	15	
Green coke	10	0.5	3	5	
Woodchips	33	1	1	60	
Electrode	0	2	10	10	
Quartzite A	0	0.8*	2	10	
		*non-SiO ₂ oxyde			

Table 2: Raw materials in conventional charges

Components	Kg / tSi	Ash	В	Р
components	Ng / 131	%	ppm	ppm
Charcoal	600	1.2	3	133
Coal	300	0.4	11	3
Char	300	0.6	17	4
Green coke	50	0	0	0
Woodchips	2000	2	2	80
Electrode	100	0	1	1
Σ from C materials		4.2	33	221
% in Si metal			90	10
In Si from C materials			30	22
From Quartzite A	2500	2.0	5	25
% in Si metal			90	50
In Si from Quartzite A			5	13
Total in Si			35	35

Table 3: B and P in Si metal with conventional charges

In the Table 3, the option of an equal weight proportion of coal based and charcoal material together with a limited amount of low reactivity green coke but a significant amount of woodchips is taken. For the quartzite that is containing some P, less emphasis was given to its purity as the major contributor to the P contamination of the metal remains the wood based reduction materials.

With charcoal, coal and char as main reduction materials in conventional charges a content of 35 ppm of both elements B and P is found in the MG-Si metal. With such a high level of these critical elements for the efficiency of the PV cells little can be done in the selection of more expensive purer raw materials so that emphasis remains the selection of cheap raw materials.

Carbosil composite briquettes in the charge

With the *Carbosil* briquettes, having the potential to provide a preferred upgraded Si metal (UMG-Si) for the solar application, the situation changes and some leeway on the cost aspect can be given. For instance washed coal and purer green cokes can be integrated into the briquettes (Table 4). Quartz sand and quartzite low in P, but also half of woodchips thanks less SiO trapping needs from the lower velocity reaction gas, help to control the P contamination. The maximisation of petcoke, which is much higher than in the in the conventional charge and this without operation and yield drawbacks, is however decisive for reducing the contamination of both elements B and P. The selection of coal is also made according the petrographical properties to ensure high reactivity of the corresponding char ^{12, 16, 17}.

		Dry basis				
Raw materials	Moisture %	Ash %	B ppm	P ppm		
Coal washed	10	0.5	10	5		
Green coke	10	0.2	2	3		
Coal tar pitch	0	0.2	3	3		
Woodchips	33	1	1	60		
Electrode	0	0.5	2	3		
Quartzsand	0	0.3*	0	1		
Quartzite B	0	0.4*	1	5		
		*non-SiO ₂ oxyde				

Table 4: Raw materials with Carbosil in the charge

Components	Kg / tSi	Ash	в	Р
components	Ng / 131	%	ppm	ppm
Carbosil Carbon	1000	0.5	8	5
Woodchips	1000	1.0	1	40
Electrode	100	0	1	1
Σ from Carbosil Carbon		1.5	10	46
% in Si metal			90	10
In Si from Carbosil Carbon			9	5
From Quartzsand	1000	0.3	0	1
From Quartzite B	1500	0.6	1	8
% in Si metal			90	50
In Si from Quartzite B			1	5
Total in Si			10	10

Table 5: B and P in Si metal with *Carbosil* Briquettes

With this scenario of 2 tons of *Carbosil*, providing one ton each of C and SiO₂, together with 1.5 ton of quartzite a contamination of 10 ppm only is obtained for both B and P elements (Table 5). This metal, with 3 to 4 times less B and P than with conventional charges, meets the requirement of UMG-Si. The purity of the produced Si reaches 99.7 %.

Costs and savings with the Carbosil briquettes

Production costs of Si metals related to the raw materials

We consider here a cost comparison with 2012 market prices of raw materials (Table 6) for a western world environment. In the costs of the *Carbosil* briquettes the capital and working capital costs represent 12 % of the investment i.e. 50 \$/t and the manpower costs amount to 40 \$/t. The tables 7 and 8 show that the cost related to the charge with *Carbosil* are marginally higher (50 \$/t Si) than those with a conventional loose charge. This is due to the fact that the usage of charcoal and char in conventional charges is expensive as similar thermal process than the one used with *Carbosil* briquettes are needed for their production but also to the fact that the low cost green coke can be maximized in the briquettes.

Local conditions can differ from this scenario especially when the production of charcoal and quartzite are integrated into the Si plant. However the investment level for the briquette plant and the costs of the *Carbosil* briquette are quite attractive especially when considering the potential savings related to the simplifications brought to the refining step.

Conventional raw materials	\$/t	\$/t Cfix
Charcoal	600	860
Coal	300	500
Char	780	860
Green coke	400	440
Woodchips	80	530
Quartzite A	120	-

Table 6: Market prices (on site) of conventional raw materials

Conventional	\$/t Cfix	\$/t	t	cost \$/tSi
Charcoal	860	600	0.6	360
Coal	500	300	0.3	90
Char	860	770	0.3	230
Green coke	440	400	0.05	20
Woodchips	530	80	0.2	160
Quartzite A		120	2.5	300
Total charge				1160

Table 7: Production costs related to a conventional charge

Savings potential with Carbosil UMG-Si for SoG-Si metal

The savings depend on the refining mode used and on the specifications set for SoG-Si. Assuming a 1ppm specification ^{18, 19, 20} means that we have to compare the refining costs for decreasing the B and P from the 35 ppm level in MG-Si with the classical charge to those for decreasing from the 10 ppm level in the UMG-Si obtained with the *Carbosil* charge.

The different routes, existing at various scales of production²¹, are the Elkem Solar, the 6N Silicon, the Photosil and the Renew Energy. The Elkem unit in Norway (5000tpy) has three sequential purification steps that are slag treatment, leaching and eventually solidification, where impurities are ultimately lowered by segregation³. The 6N Silicon process includes the dissolution of the MG-Si in Al, for improving the segregation of impurities during a first crystallisation process, a washing with acids followed by a second crystallisation to complete the elimination of the Al and left impurities²². The Photosil pilot concept involves two segregation steps followed by an ultimate plasma treatment²³. Renew Energy Co combines slag treatment, two Plasma process and two solidification steps²⁴.

All these processes are proprietary and cost breakdowns are difficult to get but all have in common at least one segregation step where the reduction of B and P from 35 to 10 ppm in the incoming metal have substantial impact. For reaching 1 ppm, with at each step an average decrease of a factor three in B and P, three steps with MG-Si and only two with *Carbosil* UMG-Si are needed. Therefore in this case the order of magnitude of savings can be estimated to be about 1/3 of the target cost of SoG-Si (15 \$/Kg) i.e. 5 \$/kg corresponding to a 4 % lower cost of the W_p. Alternatively the number of process steps can remain unchanged so that a better purity of the metal used in the PV can be obtained. This results in the worst case to about 0.5 % better cell efficiency that will lower the costs of the W_p by the same amount of 4 %.

In summary: for the production of SoG-Si the usage of UMG-Si produced with the *Carbosil* briquettes will increase the raw material cost by about one tenth of \$/kg but will eventually save several \$/kg in the production costs of SoG-Si.

	\$/t	t	cost \$/tSi
Briquettes	460	2.0	920
Woodchips	80	1.0	80
Quartzite B	140	1.5	210
Total charge			1210

Table 8: Production costs related to the Carbosil in the charge

Year	Polysilicon	SoG - Si	For PV	GW _p /y	t Si/MW _p
	tpy	tpy	tpy		
2000	20'000	0	2'000	0.1	20
2010	200'000	1'000	60'000	5	12
2020	Total	500'000	240'000	30	8

Table 9: Demand of Si for PV (20%/y growth of power and 4%/y decrease of specific. Si PV consumption)

The use of UMG-Si could also offer a second chance to lower cost purifying techniques like the one used for the preparation of 5 N Si by Timminco²⁵. We consider that the direct routes from purified raw materials²⁶ or with pure SiC ²⁷ to SoG-Si as much more difficult to apply industrially and eventually more expensive than the combination of UMG-Si production with *Carbosil* briquettes combined with simplified refining.

Industrial Carbosil plant

The co-carbonization concept for the manufacture of composite briquettes has been validated at the pilot scale. Semi-industrial production trials using existing installations in order to confirm the behaviour and performance of the *Carbosil* in full size arc furnaces are needed. Up-grade of existing paste plant and retorts have to be performed at reasonable costs. The impacts of the UMG-Si metal on the production costs of SoG-Si and on PV cells and eventually on the costs per installed W_p have to be assessed so that an economical feasibility study can be finalized.

The size of the industrial *Carbosil* plants is a function of the demand of the PV sector that is influenced by many parameters. In the Table 9, the last decade evolution is shown. In 2010 the worldwide installed solar power figure was 50 times higher than in 2000. The first production dedicated to SoG-Si has been precisely started in 2010 only so that the majority of the Si used for this application is still expensive polysilicon. At a conservative power growth rate of 20 % /y the PV demand will be above 200'000 tpy of SoG-Si, taking into account the continuous reduction of the layer thickness of the cell made with Si.

For responding to this demand, and even to accelerate it, the production of UMG-Si by *Carbosil* shall be made at a large scale. With a 50'000 tpy *Carbosil* unit, which is in line with the current capacity of one industrial retort, 25'000 tpy of UMG-Si can be produced. This corresponds to 10 % of the 2020 estimated requirement. A smaller unit can be contemplated as well as the negative impact on the production costs of the briquettes are not decisive compared to the huge saving potential in the refining costs.

Conclusions

In the race towards the investment cost reduction of PV cells below 1/ W_p the direct production of UMG-Si in arc furnaces using high purity *Carbosil* briquettes plays an important role. A better purity of the SoG-Si, meanings a higher PV efficiency, reduces the investment costs and can bring the electricity generation to a competitive level for large scale power plants.

The pilot scale works have resulted in a plant basic design that can be fine tuned after semi-industrial trials have been performed.

The ideal partner embarking into such a project is a metallurgical Si producer having already developed a refining route for the preparation of SoG-Si, a partner that is naturally eager to lower the refining production costs and to expand its production.

The collaboration with world class coal washing plants and high purity quartz sand producers can be contemplated as well. The access to an appropriate paste carbon plant remains mandatory for the validation phase where semi-industrial lots are tested and is a must for a smooth industrialization of the composite briquette dedicated to the production of UMG-Si. The ideal feedstock for a low cost SoG-Si production.

References

1. A. Schei et al.," High silicon alloys ", Tapir Forlag, ISBN 82-519-1317-9, 1998

2. D.Lynch," Winning the Global Race for solar Si ", JOM Vol. 61, No.11, 2009, pp.41-48

3. K.Peter et al.," Future potential for SoG-Si feedstock from the metallurgical process route", Proceedings of the 23rd EU Photovoltaic solar energy conference, Valencia, 2008

4. S.Dubois et al., Crystal Clear workshop on solar grade silicon feedstocks specifications, Amsterdam, 2008

5. E.H. Myrhaug and H. Tveit.," Material Balances of trace elements in the ferrosilicon and silicon processes", Electric furnace conference proceedings, pp. 591-604

6. J. Dégoulange," Purification et caractérisations physicochimiques et électriques de silicium d'origine métallurgique destiné à la conversion photovoltaïque ", Thèse à l'Institut national polytechnique de Grenoble, 2008

7. J.K. Tuset and O.Raaness,"Reactivity of reduction materials for the production of silicon, silicon-rich ferroalloys and Silicon carbide", Electric furnace conference St.-Louis, Innovation and improvement in metallurgical practices-Ferroalloys-II, Vol. 34, 1976, pp.101-107

8. A. Schei and S.A. Halvorsen, "A stoïchiometric model of the silicon process "Proceedings of the international symposium arranged in honour of Ketil Motzfeldt, May 24th 1991, pp. 41-56

9. T. Videm," Reaction rate of reduction materials for the (ferro)silicon process", Infacon 7, June 1995, pp.221-230

10. F.H. Beckmann and A.Wagner," ANCIT- Formed coke and formed blend cokes by hot briquetting", Laborlux pamphlet

11 G.W. Lask and N. Ruuth," Development and use of Silgro Carbon-silica briquettes in silicon furnaces", Aimcor pamphlet

12. T. Videm Buo et al., Reactivity and petrography of cokes for ferrosilicon and silicon production", International journal of Coal Geology, (43), 2000, pp.243-256

13. J.C. Fischer and R. Perruchoud," Kalzinierung von Briketts", CH National Patent Nr 694271, 1rst September 2009

14. G. Skodras and P.S. Amarantos, "Overview of low temperature carbonisation", CERTH-ISFTA report, 2002

15 K. Barland,"Final report-The trace element project", Miljolaboratoriet i Telemark, 2000

16. O. Raaness and R. Gray," Coal in the production of silicon rich alloys", Infacon 7 June 1995, pp.201-219

17. V. Myrvagnes and L. Lindsad," The importance of coal and coke properties in the production of high silicon alloys", Infacon XI, 2007, pp. 402-413

18. D.Sarti and R.Einhaus," Silicon feedstock for the multicrystalline photovoltaic industry", Solar energy materials solar cells, 72, 2002, pp 27

19. B.Ceccaroli and O. Lohne," Solar grade silicon feedstock", in Handbook of Science and Engineering, John Wiley, 2003, pp.177

20. A.A. Istratov et al.," Control of impurities in" dirty" multicrystalline silicon for solar cells", Materials Science and Engineering, B 134, 2006, pp.282-286

21. A.F.B. Braga et al., "New processes for the production of solar-grade polycrystalline silicon : A review", Solar Energy Materials and Solar Cells, 2007,

22. K. Petter," Materialaspekte multikristalliner Solarzellen aus UMG-Si Feedstock", FAHL Academia, Oppurg, 29th September 2009

23. R.Einhaus et al. "Photosil- Simplified production of solar silicon from metallurgical silicon 21st European photovoltaic solar energy conference, 2006

24. Renew Energy Co., Ltd , Corporate Summary Presentation

25. D. Leblanc and R. Boisvert," Process and apparatus for purifying silicon", Timminco publication, 2008

26 K.L. Sandvik and R.B: Larsen, "Silicon raw materials for the norvegian solar cell industry", 2008

27 L.J. Geerligs et al." Solar-grade silicon by a direct route based on carbothermic reduction of silica : requirements and production technology", 12th Workshop on crystalline Silicon solar cell materials and processes, Breckenridge, 11-14th August 2002, pp. 215-219