# Extending Horizon of Materials Processing with Solar Furnace -Solar-synthesis of raw material powders (carbides and carbonitrides) and solar-sintering of ceramic powder compacts with novel prospects of introducing unstable chemical species into the reaction system-

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## Abstract

Solar furnace (SF) yielding high flux of concentrated solar beam has been used for our recent trial syntheses of carbides and carbonitrides of Si and *d*-group transition metals and, during the course of this series of preliminary work, we encountered several intriguing phenomena which cannot be interpreted in terms of available equilibrium phase relationships. These new evidences seem to indicate still unexploited potentiality of solar furnace as novel type of chemical reactor rather than mere ecological heat source replacing traditional electric furnace. Besides these raw materials powder synthesis experiments, we have been testing also potentiality of SF as a reactor for sintering oxide and non-oxide ceramic powders and found that mechanical properties of the solar-sintered specimen were comparable to those of the counterpart manufactured by traditional industrial sintering process. As such, data gathered so far implicate great potentiality of SF as new type of chemical reactor. Introduction of unstable chemical species, such as non-graphitic carbon and $NH_3$ gas with suppressed degree of dissociation, into the reaction system might further extend the range of producible materials in the SF. Thus, some review is also given concerning recent works involving usage of unstable chemical species emerging from a group of Osaka University.

## 1. Introduction

Since 1997, we had opportunities to use SF (solar furnace) at PSA (Plataforma Solar de Almería). Making full use of available beam time, we undertook a series of solar-synthesis experiments of carbide and carbonitride of Si and *d*-group transition metals (excluding Hf) over 1997 - 2001 and the results obtained were presented at earlier meetings of this series (Cruz Fernandes *et al.*, 1997; Amaral *et al.*, 1998; Guerra Rosa *et al.*, 2001) as well as in form of open literature (Cruz Fernandes *et al.*, 1998 and 1999; Guerra Rosa *et al.*, 1999; Martínez *et al.*, 1999; Shohoji *et al.*, 1999 and 2000; Amaral *et al.*, 2000; Rodríguez *et al.*, 2001). The results obtained so far revealed intriguing potentiality of solar furnace as a new reactor for synthesising materials, which cannot be produced by traditional industrial or laboratory process.

Besides these raw material powder production experiments at PSA, we also carried out mechanical properties evaluation for solar-sintered compact of oxide and non-oxide ceramic powders prepared using solar furnace at Uzbek Academy of Sciences (Tashkent, Uzbekistan). Results obtained in this series of works demonstrated that, in spite of very rapid heating and cooling rates applied during the solar-sintering, mechanical properties of the solar-sintered ceramic powder compact were comparable to those of the counterpart manufactured by traditional sintering process with slow rates of heating and cooling (Cruz Fernandes *et al.*, 2000; Guerra Rosa *et al.*, 2002; Amaral *et al.*, 2002).

Considering informal nature of this workshop, we would like to present background philosophy of our work which was not written in explicit fashion in our earlier publications rather than to review merely the results obtained which might be referred to easily in the open literature. Then, we would like to propose further investigations to be done in this line of work.

## 2. Solar synthesis of carbides

Most significant aspect in our series of work done for solar-carbide synthesis was employment of amorphous carbon (aC) besides graphite (G) as the carburising medium. In some solar-synthesis experiments of carbides, reaction product obtained with aC was not exactly the same as the one obtained with G under otherwise comparable experimental conditions (Cruz Fernandes *et al.*, 1999; Guerra Rosa *et al.*, 1999; Amaral *et al.*, 2000; Rodríguez *et al.*, 2001).

For example, Cruz Fernandes *et al.*(1999) reported that $TiC_x$ with composition $x$ closer to the equilibrium composition was prepared from compact of Ti powders mixed with excess aC powders (aC/Ti mole ratio in the starting material was set to be 1.5 to ensure co-existence of free carbon with the formed $TiC_x$ at the end of the reaction) after 30 min solar radiation which heated up the specimen to around 1600°C whereas the reaction of Ti with G looked somewhat slower than the reaction of Ti with aC under the comparable experimental conditions. These results were understandable with reference to the anticipated kinetic effect of aC. That is, higher chemical activity $a$(C) of aC with reference to that of G would result in the reaction rate acceleration (kinetic effect) as well as the shift of equilibrium point for non-stoichiometric carbides $MC_x$ towards higher $x$ side compared with the reference $x_0$ reached with G (equilibrium effect) (Katsura *et al.*, 1971, 1975 and 1992; Nomura *et al.* 1973<a> and 1973<b>; Shohoji, 1977; Shohoji *et al.*, 1990).

Concerning the equilibrium effect of $a$(C) level, what we observed in the solar-synthesis of Mo carbide was somewhat surprising showing evidence of promoted formation of higher mono-carbide $MoC_{1-x}$ of Mo besides sub-carbide $Mo_2C$ under co-existence with G but not with aC during 30 min solar irradiation yielding $T = 1600^{\circ}C$ (Guerra Rosa *et al.*, 1999). The result would have looked more rational if the mono-carbide of Mo formed with aC rather than with G.

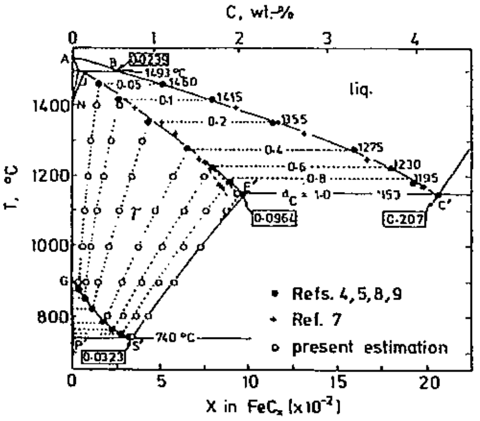
Similarly puzzling result was obtained in the solar-carburisation of V (Amaral *et al.*, 2000). In this case, unexpected formation of sub-carbide $V_2C$ besides mono-carbide VC took place under the solar-radiation for the specimen with aC rather than for the specimen with G. In these two cases for Mo and V, observed experimental evidences indicated that aC yielded effective $a$(C) lower than that of G for the carburisation under the solar radiation.

These apparently peculiar results indicated the inherently complicated nature of solar materials synthesis in which the phase equilibrium cannot be determined uniquely as functions of chemical activities of the reactants and temperature alone but another factor representing wave spectrum of radiation in solar beam must be taken into account (Rodríguez *et al.*, 2001). To elucidate this aspect, we are planning to develop an SF optical system integrated with filter to cut certain range of wave length with the aim of identifying frequency range of radiation causing certain unexpected effects (we believe it must be of some photochemical nature).

In the following, why we used aC as well as G as the carburising medium in the solar materials synthesis experiments is explained in some detail.

## 2.1 Graphite and amorphous carbon

Thermodynamically stable form of carbon C in solid state is graphite G. Thus, $a$(C) of G is defined as 1. Diamond and any other allotropic form of carbon in solid state is with $a$(C) greater than 1. On the other hand, $a$(C) smaller than 1 can be realised, for example, by using mixture of CO and $CO_2$ gas through control over partial pressure ratio, $p(CO)/p(CO_2)$. **Fig. 1** shows binary Fe-C equilibrium phase relationship compiled by Hansen and Anderko (1958) added with constant-$a$(C) curves estimated from statistical thermodynamic analysis results (Shohoji, 1987). As seen in this plot, composition $x$ of $\gamma$-$FeC_x$ in single-phase region is determined uniquely when both temperature $T$ and $a$(C) are specified. For example, when $\gamma$-$FeC_{0.05}$ is desired to be prepared at 900°C, $a$(C) = 0.8 must be used while $a$(C) = 0.4 is sufficient for preparation of $\gamma$-$FeC_{0.05}$ at 1200°C.



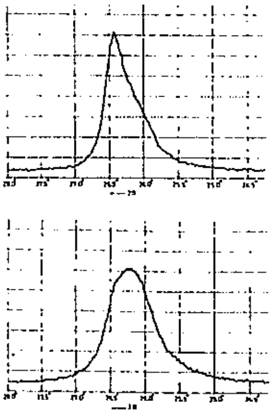


Fig. 1 Binary Fe-C equilibrium phase diagram superimposed with the constant-$a$(C) curves estimated on the basis of statistical thermodynamic analysis results (reproduced from Shohoji, 1987).

Fig. 2 Typical X-ray diffraction (XRD) pattern of (002) index for the free carbon precipitated from the reaction of UC + $N_2$ (top) and that of the carbon from $UC_2$ + $N_2$ (bottom) at 1300°C under $p(N_2)$ = 700 mmHg (reproduced from Nomura *et al.*, 1973<b>).

Graphite yields sharp intense (002) XRD (X-ray diffraction) peak at $2\theta$ = 26.5° with CuK$\alpha$ radiation while no clear XRD peak emerges for amorphous carbon. Depending on the degree of graphitisation of non-graphitic carbon, XRD peak position $2\theta$ and half-width $B_M$ as well as peak geometry would vary. **Fig. 2** reproduces XRD C(002) peaks obtained for free carbon precipitated from reaction of UC + $N_2$ (top) and that from $UC_2$ + $N_2$ (bottom) at 1300°C under nitrogen partial pressure $p(N_2)$ = 700 mmHg (reproduced from Nomura *et al.*, 1973<b>). In fact, observed patterns of variations of $2\theta$ and $B_M$ with respect to the reaction conditions, $T$ and $p(N_2)$, were regular for the free carbons precipitated from the reaction UC + $N_2$ as summarised in **Fig. 3**.

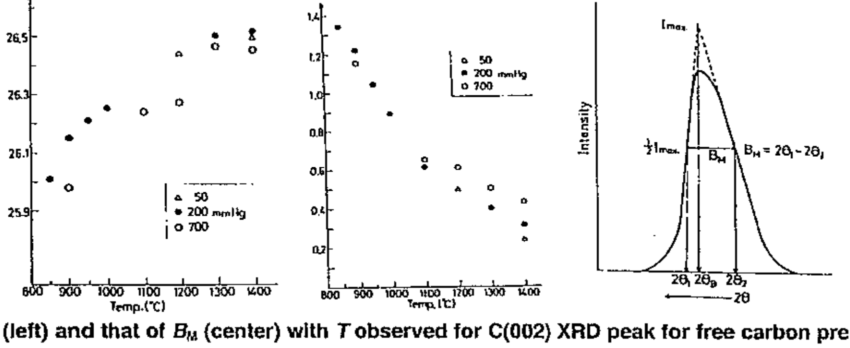


Fig. 3 Variation of $2\theta$ (left) and that of $B_M$ (center) with $T$ observed for C(002) XRD peak for free carbon precipitated from UC + $N_2$ at varying $p(N_2)$ and schematic method for determining $2\theta$ and $B_M$ (right) (reproduced from Nomura *et al.*, 1973<b>).

## 2.2 Accelerated graphitisation of aC with W or Cr under solar radiation

Non-graphitic carbon species are not stable thermodynamically and thence, by heating to temperature higher than 1500°C, they are subjected to graphitisation process to be converted eventually to graphite after certain period (typically, several hours for XRD (002) peak to become discernible).

However, we observed emergence of clear C(002) peak from aC mixed with W or Cr (aC/M ratio set at 1.5) and irradiated by solar beam in SF at PSA for 30 min (Shohoji *et al.*, 1999 and 2000). This extent of rapid aC graphitisation was not anticipated and, being intrigued by these results, we repeated our solar-radiation experiments with W at varying aC/W ratios, 1.5, 2.5, 5 and 10, in July 2001 using SF at PSA. The aim of this test run was to check up to which aC/W ratio the aC graphitisation could be realised. Accepting that aC graphitisation proceeded over W (or WC) surface by some photochemical catalytic effect, we guessed that there must be some threshold aC/W level for the entire aC mixed with W to be subjected to graphitisation. We wanted to determine this threshold level by the recent experimental run for the aC/W mixtures.

To our surprise, no peak developed at C(002) position. We are now trying to identify the cause for this lack of reproducibility in the aC/W experiment. One of suspicious factors is the quality of used paraffin as the compacting aid. In the preparation of aC/M powder mixture compact, it is a common practice to add paraffin as binder because of lacking adhesion among mixed powder particles when aC powders are present. In the carburising reaction undertaken in electric furnace, no evidence of promoted graphitisation of aC was detected with U, Ce and other *d*-group transition metals at reaction temperature 1600°C up to reaction period 20 h or longer (Katsura *et al.*, 1975; Shohoji, 1977; Shohoji *et al.*, 1990). In these earlier works, paraffin in solid form at ambient temperature was added to the powders mixture in form of melt (by heating). In the earlier solar-carburisation experiments for W and Cr with aC (Shohoji *et al.*, 1999 and 2000), the same solid paraffin was added in form of melt to the powders mixture but, in the July 2001 test run, aC/W mixture was pressed into pellet by adding paraffin in liquid state at ambient temperature. Anyway, we cannot rule out other possibilities leading to the experienced lack of the reproducibility of the aC/W experiments. One of such possibilities is the demand to exceed certain threshold temperature for the aC graphitisation reaction to proceed over W (or WC) even under the solar radiation. In the earlier experiments, temperature reached was 1600°C but, due to ageing deterioration of reflectors in the optical system of SF at PSA, temperature failed to reach 1500°C in the July 2001 experiments. Another possibility is the natural wave spectrum fluctuation in the solar beam. If the involved reaction is with certain photochemical nature, it would demand trigger with some wave of preferential frequency and the intensity of such wave was insufficient in the July 2001 test run. At this moment, we do not know what is exactly the cause leading to the lacking reproducibility of the aC/W experiments.

## 3. Solar-sintering of ceramic powder compacts

Feasibility of manufacturing consolidated bodies from ceramic powder compacts by solar-sintering was tested using SF at Uzbek Academy of Sciences (Tashkent, Uzbekistan) for both oxide ceramics (alumina) (Cruz Fernandes *et al.*, 2000; Amaral *et al.*, 2002) and non-oxide ceramics (WC-Co) (Guerra Rosa *et al.*, 2002).

The results obtained so far looked encouraging (see **Table 1** and **Table 2**) suggesting promising applicability of solar-sintering for production of consolidated ceramic powder bodies. In fact, there was slight worsening of mechanical properties detectable for the solar-sintered ceramics disk specimens compared with those for the counterparts manufactured by the traditional industrial process on account of the rapid rates of heating and cooling (specially, cooling) involved in the solar-sintering. Anyway, noting realised reduction of manufacturing time by more than one order of magnitude by the solar-sintering compared with that of the traditional industrial sintering process (see, for example, Fig. 1 in Guerra Rosa *et al.*, 2002) and the resultant manufacturing cost reduction per piece, slight worsening of mechanical properties and the consequent service life shortening of the component manufactured by solar-sintering might be considered acceptable in some areas of applications.

**Table 1 Measured density ρ and estimated values for the porosity *p* and Young's modulus *E* for the alumina disk specimens (reproduced from Amaral *et al.*, 2002).** CR: cooling rate

| Properties | Electric furnace | Solar furnace | |
|---|---|---|---|
| | CR = 20 K/min | CR = 30 K/min | CR = 50 K/min |
| ρ (g/cm$^3$) | 3.83 ± 0.00 | 3.87 ± 0.01 | 3.85 ± 0.02 |
| *p* (%) | 3.20 ± 0.01 | 2.38 ± 0.14 | 2.71 ± 0.44 |
| *E* (GPa) | 361.5 ± 0.1 | 374.2 ± 2.2 | 369.0 ± 6.8 |

**Table 2 Density, Vickers micro hardness and fracture toughness values measured for the sintered WC-10 mass% Co specimens (reproduced from Guerra Rosa *et al.*, 2002).**

| Specimen | Medium Density ρ (g/cm$^3$) | Vickers Hardness Hv (GPa) | Fracture Toughness $K_{IC}$ (MPa m$^{1/2}$) |
|---|---|---|---|
| Solar | 14.3 ± 0.3 | 13.14 ± 0.96 | 12.3 ± 1.5 |
| Conventional | 14.5 ± 0.2 | 12.56 ± 0.11 | 14.2 ± 0.8 |

## 4. Proposals for future development of solar materials processing

As we reviewed above, SF proved to work all right for sintering of the ceramic powder compacts (either oxide or non-oxide ceramics) as well as for raw material powder synthesis of carbides and carbonitrides. Several intriguing effects of photochemical nature appeared to be in function during the reaction process under solar beam radiation. As typical for photochemical effects, some effect tend to emerge selectively only for certain combinations of starting materials. Systematic understanding for this aspect with reference to electron energy level information of materials would be essential towards efficient use of SF for advanced materials processing. This is, in fact, the broad long-term target of this line of investigation.

On the other hand, our immediate short-term targets in this line of work are clarification of doubts arisen during the recent series of works;

1) Identifying cause for the lacked reproducibility in the graphitisation experiments of aC with W under solar radiation (terms to be checked include quality of paraffin added as binder, threshold temperature for aC graphitisation and spectrum of solar beam).

2) Higher carbide formation for Mo with G under solar radiation.

3) Sub-carbide formation for V with aC under solar radiation.

Our medium-term research plan in the solar materials processing includes introduction of unstable chemical species, like aC and un-cracked $NH_3$, which might yield higher chemical activity than that of the stable form of the element (G and diatomic $N_2$ and $H_2$, respectively) into the reaction system. In laboratory experiments using the traditional electric furnace as the heat source, the effects of unstable chemical species in the reactants on the reaction products were extensively investigated by Katsura and his co-workers (Katsura *et al.*, 1971, 1975, 1992, 1998<a>, 1998<b>; Katusra, 1991, 1992; Katsura and Serizawa, 1992; Katsura and Miyake, 1993; Nomura *et al.*, 1973<a>, 1973<b>; Yoshizawa *et al.*, 1977; Shohoji, 1977; Shohoji *et al.*, 1990; Hirota *et al.*, 1993; Urabe *et al.*, 1993; Nishimaki *et al.*, 1998<a>, 1998<b>).

By employment of aC, modest $a(\mathrm{C})$ rise by less than one order of magnitude might be gained but, according to theoretical analysis by Katsura (1991, 1992), significant $a(\mathrm{N})$ rise by as great as $10^6$ order might be realised by suppressing dissociation of $NH_3$ by flowing it in the reaction system with reference to $a(\mathrm{N})$ of the stable diatomic $N_2$ gas ($= p(N_2)^{1/2}$) (see **Fig. 4**). For example, by using extremely high $a$(N) of flowing $NH_3$ gas, mono-nitride MoN can be synthesised at relatively low temperature under normal pressure (Shohoji, 1977; Yoshizawa *et al.*, 1977; Shohoji *et al.*, 1990) while MoN cannot be prepared with $N_2$ gas at pressure as high as 300 bar (only sub-nitride $Mo_2N$ formed) (Jehn and Ettmayer, 1978).

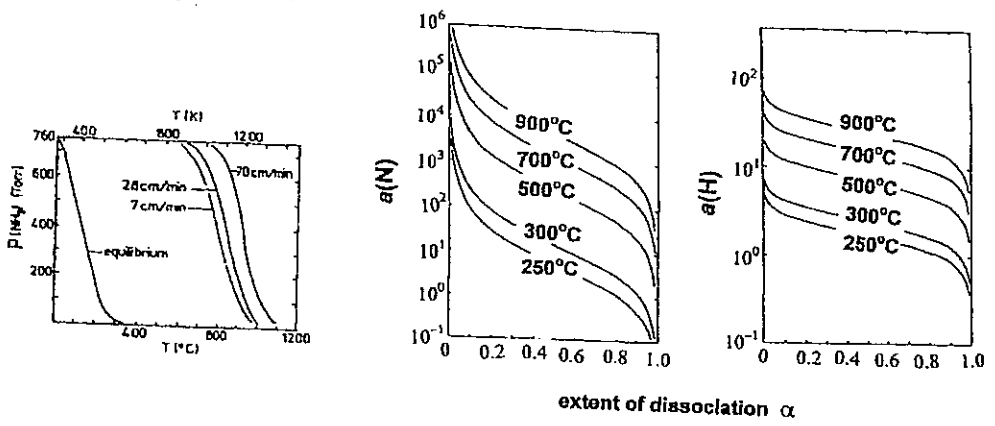


**Fig. 4** (from left to right) Partial pressure $p(NH_3)$ of $NH_3$ gas in the alumina reaction tube (– 30 mmφ) under total pressure 1 atm; equilibrium curve by calculation and $p(NH_3)$ under flow conditions by gas chromatographic measurement (reproduced from Shohoji *et al.*, 1990): Relative nitrogen activity $a$(N) exhibited by flowing $NH_3$ as a function of extent of dissociation α at several temperatures $T$ and relative hydrogen activity $a$(H) of $NH_3$ as a function of α at several $T$ (reproduced from Katsura, 1992).

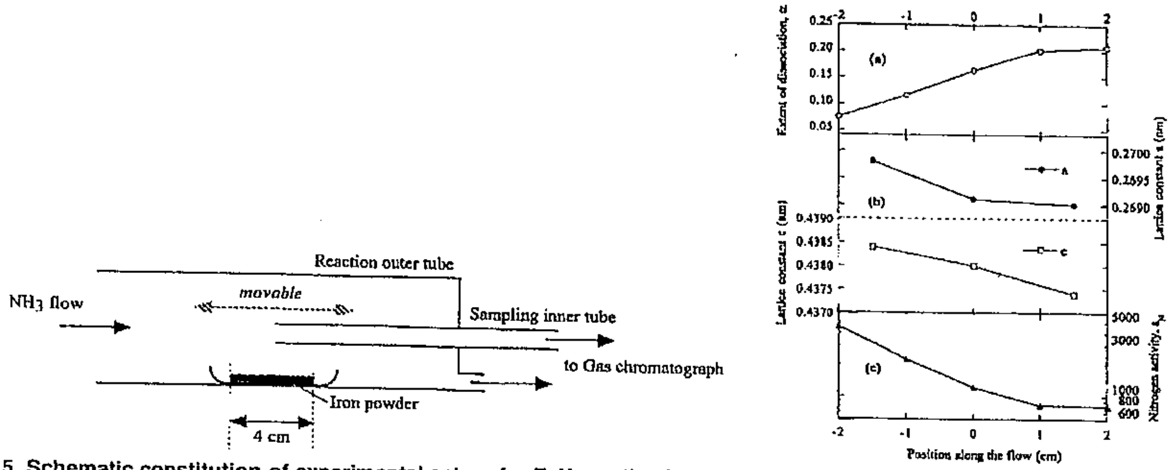


**Fig. 5** Schematic constitution of experimental set-up for $FeN_x$ synthesis under flowing $NH_3$ gas at varying positions along the flow and the obtained results plotted as a function of the position along the gas flow; (a) extent α of dissociation of $NH_3$: (b) lattice constants, $a$ and, $c$ of the formed ε-$FeN_x$: (c) calculated $a$(N) of the gas phase (reproduced from Nishimaki *et al.*, 1998<a>).

As $a$(N) of $NH_3$ gas varies depending on the duration of exposure of $NH_3$ gas to certain temperature $T$, $a$(N) gradient along the $NH_3$ gas flow path is generated and, accordingly, $FeN_x$ of varying $x$ was reported to be synthesized under flowing $NH_3$ gas by placing the Fe powders at different locations of the horizontal furnace tube (see **Fig. 5**; Nishimaki *et al.*, 1998<a>, 1998<b>). As clearly seen in Fig. 5, extent of dissociation α of flowing $NH_3$ gas tended to rise on going from the left (up-stream side) to right (down-stream side) in the depicted experimental set-up and, accordingly, $a$(N) of the gas phase (un-cracked $NH_3$ molecules) and $x$ in ε-$FeN_x$ phase formed tended to drop on going from the up-stream side towards the down-stream side. In a recent publication, Katsura *et al.*(1998<a>) reported that $CH_4$ gas was generated under $NH_3$ gas stream only from aC but not from G reflecting the high $a$(C) of aC. In this case, what made the yield of $CH_4$ possible was concluded to be the high $a$(H) of the un-cracked $NH_3$ gas molecule as well as the high $a$(C) of aC. As the time elapsed in this experiment, rate of $CH_4$ yield from aC was observed to decline (Fig. 4 in Katsura *et al.*, 1998<a>) on account of progressing aC graphitisation with time (Fig. 1 in Katsura *et al.*, 1998<a>).

As such, introduction of unstable chemical species like aC and $NH_3$ into the reaction system under solar beam radiation might extend further the horizon of the solar-materials processing to lead to formation of novel products which cannot be manufactured under traditional industrial or laboratory processing conditions, at least under certain limited circumstances. Anyway, as represented by the above examples, high chemical activity of the element in the unstable chemical species might vary as a function of time as well as a function of spatial position in the reaction system. This aspect must be kept in mind in the introduction of unstable chemical species into the reaction system with solar beam as well as into the traditional laboratory or industrial reaction system.

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