

Theoretical screening and synthesizing sorbent materials for capturing CO₂ and oxidizing CO to CO₂

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ABSTRACT

Since the current technologies for capturing CO₂ are still too energy intensive, to develop new materials that can capture CO₂ reversibly with acceptable energy costs are still needed. In this presentation, (i) by combining *ab initio* thermodynamic calculations with database mining, we demonstrate a high-throughput screening methodology to identify most promising candidates of CO₂ sorbents from material databank; (ii) we show theoretical ways to synthesize new sorbents which could fit the needs of practical capture technologies; and (iii) we analyze some sorbents which possess dual-functionalities: as catalyst to oxidize CO to CO₂ and as sorbent to capture CO₂.

Keywords: CO₂ capture, material screening, mixed solid sorbents, *ab initio* thermodynamics, CO oxidation

1. INTRODUCTION

Nowadays, the burning of fossil fuels is still one of the main energy sources for the world's economy. One consequence of the use of these fuels is the emission of huge quantities of CO₂ into the atmosphere creating environmental problems such as global climate warming.[1-3] One approach to solve such environmental problems is to capture, utilize and sequester the CO₂. Current technologies for capturing CO₂ are still too energy intensive. Hence, there is critical need for development of new materials that can capture and release CO₂ reversibly with acceptable energy costs.

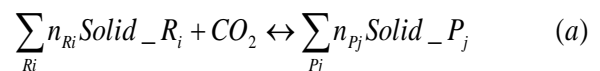
During past years at NETL, we developed a theoretical methodology to identify promising solid sorbent candidates for CO₂ capture by combining thermodynamic database searching with *ab initio* thermodynamics obtained based on first-principles

density functional theory (DFT) and lattice phonon dynamics.[4-10] The primary outcome of our screening scheme is a list of promising CO₂ sorbents with optimal energy usage.

For a practical CO₂ capture technology, it has optimal operating conditions, such as the absorption/desorption temperature range (ΔT_0). As a good sorbent, its CO₂ capture/release temperature should fit into such range. However at a given CO₂ pressure, the turnover temperature (T_t) of an individual solid capturing CO₂ reaction is fixed. Such T_t may be outside the operating temperature range (ΔT_0) for a particular capture technology. In order to adjust T_t to fit the practical ΔT_0 , in this study, we demonstrate that by mixing different types of solids, it's possible to shift T_t to the range of practical operating conditions.

2. THEORETICAL METHODOLOGY

A complete description of the computational methodology together with relevant applications can be found in our previous publications. [4-12] The CO₂ capture reactions of solids can be expressed generically in the form (for convenient description, we normalized the reaction to 1 mole of CO₂)



where n_{R_i} , n_{P_j} are the numbers of moles of reactants (R_i) and products (P_j) involved in the capture reactions. As discussed in the following section, the reactants R_i can simply be mixed solids or a newly formed solid by mixing different kinds of solids with certain mixing ratios. We treat the gas phase CO₂ as an ideal gas. By assuming that the difference between the chemical potentials ($\Delta\mu^0$) of the solid phases of reactants (R_i) and products (P_j) can be approximated by the difference in their total energies

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(ΔE^{DFT}), obtained directly from DFT calculations, and their vibrational free energies of phonons dynamics and by ignoring the PV contribution terms for solids, the variation of the Gibbs free energy (ΔG) for reaction (a) with temperature and CO_2 pressure can be written as

$$\Delta G(T, P) = \Delta \mu^0(T) - RT \ln \frac{P_{\text{CO}_2}}{P_0} \quad (1)$$

where

$$\Delta \mu^0(T) \approx \Delta E^{\text{DFT}} + \Delta E_{\text{ZP}} + \Delta F^{\text{PH}}(T) - G_{\text{CO}_2}^0(T) \quad (2)$$

Here, ΔE^{DFT} is the DFT energy difference between the reactants and products of reaction (a), ΔE_{ZP} is the zero-point energy difference between the reactants and products and can be obtained directly from phonon calculations. ΔF^{PH} is the phonon free energy change excluding zero-point energy (which is already counted into the ΔE_{ZP} term) between the solids of products and reactants. P_{CO_2} is the partial pressure of CO_2 in the gas phase and P_0 is the standard state reference pressure taken to be 1 bar. The heat of reaction ($\Delta H^{\text{cal}}(T)$) can be evaluated through the following equation

$$\Delta H^{\text{cal}}(T) = \Delta \mu^0(T) + T[\Delta S_{\text{PH}}(T) - S_{\text{CO}_2}(T)] \quad (3)$$

where $\Delta S_{\text{PH}}(T)$ is the difference of entropies between product solids and reactant solids. The free energy of CO_2 ($G_{\text{CO}_2}^0$) can be obtained from standard statistical mechanics, [6, 7, 10] and its entropy (S_{CO_2}) can be found in the empirical thermodynamic databases. [13] Eq. (1) provides the relationships of Gibbs free energy change of reaction (a) versus temperature and CO_2 pressure. Obviously, when set $\Delta G=0$, the P-T relationship (van't Hoff plot) is obtained to determine the turnover temperature T_t :

$$T_t = \frac{\Delta \mu^0(T)}{R \ln \frac{P_{\text{CO}_2}}{P_0}} \quad (4)$$

Based on this equation, at giving CO_2 pressure P_{CO_2} , the turnover temperature T_t can be determined for each CO_2 capture reaction.

It should be pointed out that this method focuses on the solid materials. However, the general principle can be applied to liquid systems by calculating the free energy of solution through DFT and molecular dynamical simulations.

3. RESULTS AND DISCUSSIONS

3.1 High-throughput screening CO_2 sorbents

Based on this theoretical methodology, for a given material databank we can screen good candidates for

CO_2 sorbents. Figure 1 shows the screening methodology.

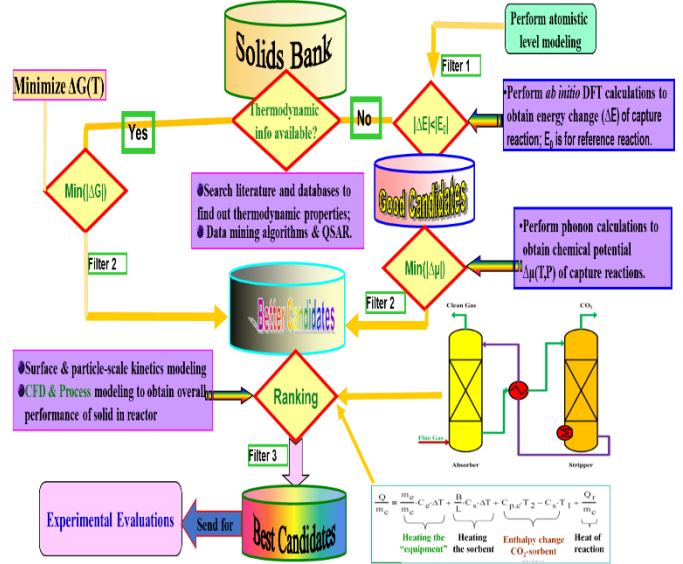


Fig. 1 High-throughput screening methodology

As illustrated in Fig. 1, for a given databank, we can manipulate our methodology as several steps:

(i) For each solid, search its available thermodynamic data from available resources (such as literature, thermodynamic database, other databases, etc.) to make initial judgment: following reaction (a), if the thermodynamic data of the solid and its corresponding carbonate and other products are available, we can minimize the free energy of its CO_2 reaction by comparing with a reference material and a free energy criteria (e.g. ± 20 kcal/mol). Once it is satisfied such criteria, we select it as better candidate. Otherwise, go back the databank to pick another compound;

(ii) If the thermodynamic data of the candidate or/and any solids involving in the CO_2 capture reaction (a), we first perform the DFT calculations for both reactants and products of CO_2 capture reaction and obtain the energy difference (ΔE^{DFT}) of the reaction. If $0.5 \text{ eV} > \Delta E^{\text{DFT}} > -2 \text{ eV}$ which covers temperature range from room-temperature to over 1000 K, we select this compound and continue to add in the free energies of CO_2 and H_2O gases obtained from standard thermodynamic Table to obtain the $\Delta E_1(T)$ for the reaction. If the $\Delta E_1(T)$ is still falling into the criteria above, we select this solid material as “good candidate”. Otherwise, go back to step (i) to pick another material from the databank. We call this process as filter I.

(iii) For those “good candidates” selected from the filter I, we perform phonon calculations for reactants and

products to obtain their zero-point energies and phonon free energy changes for their CO₂ capture reactions. According to Eqs. (1) and (2) to obtain the chemical potential ($\Delta\mu(T,P)$) of the reaction. For better candidates, their $\Delta\mu(T,P) \rightarrow 0$ (filter II) at desired working conditions (T, P). After this filter, only a short list of solids left for the given data bank;

(iv) For those “better candidates”, additional modeling (filter III) could be performed on them to rank them to obtain the “best candidates” for experimental validations. Filter III could include several modeling processes. One is the kinetics of the capture reactions, which could be done by transport and diffusion calculations as well as experimental measurements. Another necessary and doable modeling is the real behavior of solid in the reactor, which can be done by computational fluid dynamics (CFD) based on finite element method (FEM) approach. These simulations are under progressing. Application of these screening filters will ensure that only the most promising candidates will be identified for experimental testing.

As an example, Fig. 2 shows the results of applying our screening procedure to a small databank which include the alkali and alkaline metal oxides, hydroxides, carbonates and bicarbonates.[4, 6, 7, 10] As one can see that initially there are 21 possible CO₂ capture reactions. After screening, based on the reference CaO, only two materials (MgO and NaHCO₂/Na₂CO₃) are candidates which need further experimental tests.

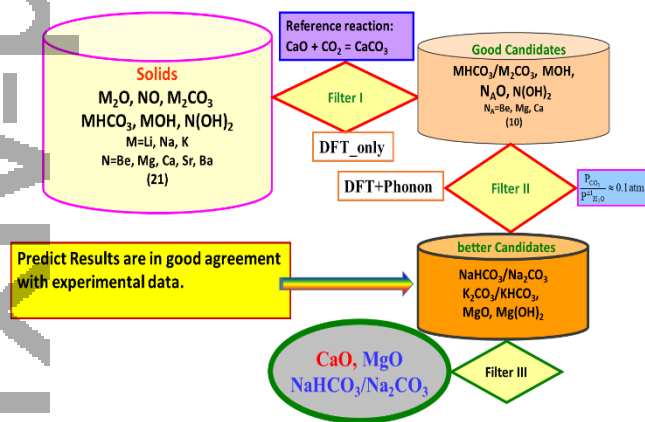


Fig. 2 Screening alkali and alkaline metal oxides, hydroxides, carbonates bicarbonates.

Using this methodology, we have explored hundreds of solid materials and several most promising candidates have been identified for experimental validations. This screening methodology provides a path for rapidly

evaluating materials for which experimental thermodynamic data are unavailable. One area where this approach could be used to great advantage is in evaluating mixtures and doped materials, where thermodynamic data are not generally available.

3.2 Synthesize new sorbent materials

As we know for a given CO₂ capture process, its optimal working conditions (CO₂ pressures of pre- and after-capture, absorption/desorption temperature range (ΔT_0), etc.) were fixed. However, at a given CO₂ pressure, the turnover temperature (T_t) of an individual solid capturing CO₂ reaction is also fixed. Hence, such T_t may be outside the operating temperature range ΔT_0 for a particularly capture technology. In order to adjust T_t to fit the practical working environments through reversible chemical transformations, the chemical properties of solids must be modified to change the $\Delta G(T, P)$ in Eq. (1). If we want to increase the T_t to high temperature range, the $\Delta G(T, P)$ should be more negative. To achieve it, we can either destabilize the reactants (sorbents) or stabilize the products or do both. On contrary, if we want to decrease T_t to low temperature range, the $\Delta G(T, P)$ should be less negative, which can either stabilize the reactant (sorbents) or destabilize the products or do both. In other words, as shown in the following Table, mixing stabilizer or destabilizer in solid could change the thermodynamic properties of their CO₂ capture reactions to shift T_t .

Table 1. Ways to shift T_t of CO₂ capture reaction

Goal on T_t	$\Delta\mu^0(T)$	$\Delta\mu_{\text{product}}^0(T)$	$\Delta\mu_{\text{reactant}}^0(T)$
Decrease	Less negative	↑ destabilize	↓ stabilize
Increase	More negative	↓ stable, lower energy level	↑ destabilize, increase energy level

As effective main CO₂ captors through chemical reactions to form carbonates, alkali and alkaline earth metal oxides are important of interests due to their easy reacting with CO₂ and low costs. The problem is that they can strongly react with CO₂ to form carbonates, but their T_t are very high and only can be regenerated at very high temperatures which are unsuitable for many CO₂ capture technologies. Hence, mixing with other solids to shift their T_t becomes important for their suitability as CO₂ sorbents.

Generally, when we mix two solids A and B to form a new sorbent C, the turnover temperature of the newly resulted system (T_c) is located between those of A and B (T_A, T_B) individuals. Here it was assumed that A is a strong

CO₂ sorbent while *B* is a weak CO₂ sorbent and $T_A > T_B$. Also, we assumed that the desired operating temperature T_O is between T_A and T_B ($T_A > T_O > T_B$). Depending on the properties of *A* and *B*, as shown in above Table we have typically three scenarios to synthesize the mixing/doped sorbent *C*:

Case I: $T_A \gg T_B$ and the *A* component is the key part to capture CO₂

In this case, by mixing *B* into *A*, a new solid *C* is formed. Since *B* does not capture CO₂, it serves as a stabilizer to stabilize *A* to form solid *C* which reaction possesses lower energy than *A* and *B* individuals. Therefore, the energy state of reactant is lower than pure *A*. therefore, less negative value of $\Delta G(T, P)$ is obtained and the mixed sorbent shifts T_t to lower temperature range. Obviously, the amount of shifted temperature depends on the mixing ratio.

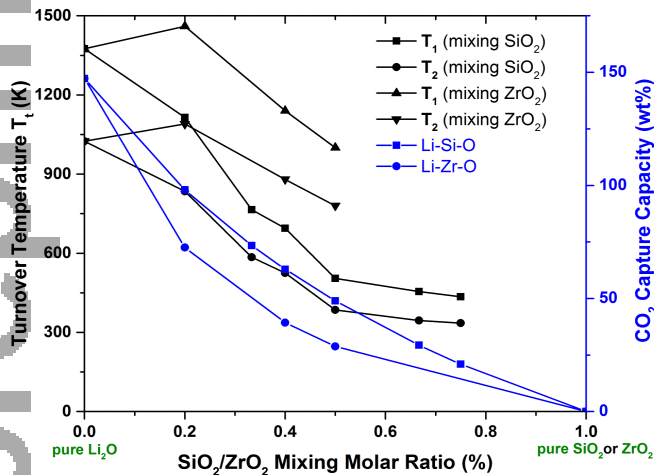


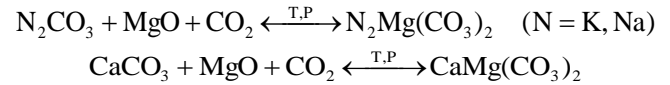
Fig. 3 The calculated T_t and CO₂ capture capacity versus molar percentage of SiO₂ or ZrO₂ in the lithium silicates or zirconates. T_1 are the turnover temperatures under pre-combustion conditions with CO₂ partial pressure at 20 bars, while T_2 are the turnover temperatures under post-combustion conditions with CO₂ partial pressure at 0.1 bar.

As an example of this case, Fig.3 shows the mixture of Li₂O/SiO₂ and Li₂O/ZrO₂. As we know the Li₂O is a very strong CO₂ sorbent which forms Li₂CO₃. However, its regeneration from Li₂CO₃ only can occur at very high temperature ($T_A \geq 1000$ K).[7] In order to move its T_A to lower temperatures, one can mix some weak CO₂ sorbents (such as SiO₂, ZrO₂). With different mixing ratio of Li₂O/SiO₂(or ZrO₂), different stable lithium silicates (zirconates) can be formed, such as Li₈SiO₆, Li₄SiO₄, Li₆Si₂O₇, Li₂SiO₃, Li₂Si₂O₅, Li₂Si₃O₇; Li₈ZrO₆, Li₆Zr₂O₇, Li₂ZrO₃, etc. Such lithium silicates and zirconates stabilize the reactants and hence decrease the T_t of CO₂ capture reaction. Detailed descriptions of these materials can be

found in previous publications.[4-7, 11, 14, 15] As one can see that by adjusting the SiO₂/Li₂O or ZrO₂/Li₂O ratios the T_t can be shifted to lower temperature range (e.g. 500-400 K). Therefore, by controlling the mixing ratio, it's possible to move the CO₂ capture temperature down to the right range required by certain capture technology.

Case II: $T_A \gg T_B$ and *B* component is the key part to capture CO₂

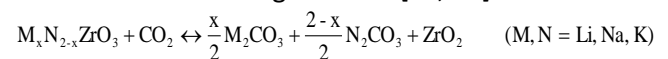
Opposite to previous case, in this case we want to increase T_t . As described above, to achieve such goal, we can either stabilize the products or destabilize the sorbents or do both to decrease $\Delta G(T, P)$ in Eq. (1) with more negative. For example, pure MgO has a very high theoretical CO₂ capture capacity. However, its T_t (~250 °C) is lower than the required temperature range of 300-470 °C used in warm gas clean up technology and its practical CO₂ capacity is very low, and therefore, it cannot be used directly as a CO₂ sorbent in this technology.[16, 17] However, by mixing other oxides or carbonates M₂O/M₂CO₃ (M=Li, Na, K) and CaO/CaCO₃, we can shift the T_t of MgO to higher temperature range through the following reactions:



As one can see that the mixed oxides/carbonates formed double salts which stabilize the products to lead more negative $\Delta G(T, P)$, and hence increase the T_t . More details on such mixture sorbents can be found in previous publications. [16, 18]

Case III: Both *A* and *B* are active for CO₂ capture

In this case, we want both *A* and *B* components are active to capture CO₂, and the CO₂ capacity of the mixture is the summation of those of *A* and *B*. As we know another potential advantage of mixing solids is to increase the surface area of the solids in order to have faster reaction rates and kinetics. Such mixing scenario doesn't show too much advantage in shifting the capture temperature, but may enhance the kinetics of the capture process and eventually make the mixtures more efficient. For example, the Li-/K- doped Na₂ZrO₃ capture CO₂ have the following reaction:[19, 20]



When the Na₂ZrO₃ doped with different molar ratio of Li or K, the thermodynamic properties of the doped systems (Na_{2-x}M_xZrO₃) are quite different from pure Na₂ZrO₃. Based on the calculated relationships among the Gibbs free energy change, CO₂ pressure and temperature for CO₂ capture reactions by Na_{2-x}M_xZrO₃

(M= Li, K, x= 0.0, 0.5, 1.0, 1.5, 2.0), compared to pure Na_2ZrO_3 , overall, the Li- and K-doped mixtures $\text{Na}_{2-x}\text{M}_x\text{ZrO}_3$ have lower turnover temperatures (T_t). The calculated results show that the shift in T_t depends not only on the doping element, but also depends on the doping level.[20] The Li-doped systems have larger T_t decreases than the K-doped systems. When increasing the Li-doping level x, the T_t of corresponding mixture $\text{Na}_{2-x}\text{Li}_x\text{ZrO}_3$ decreases further to a low temperature range. However in the case of K-doped systems $\text{Na}_{2-x}\text{K}_x\text{ZrO}_3$, although initial doping of K into Na_2ZrO_3 can shift its T_t to lower temperature range, further increasing the K-doping level x results in an increase in T_t . Therefore, compared to K-doping, lithium inclusion into Na_2ZrO_3 structure has a larger influence on the CO_2 capture performance.

3.3 Sorbents with dual-functionalities

To generate H_2 by coal gasification or methane steam reforming, the CO is further converted to CO_2 through water gas shift reaction $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$. After separation of H_2 and CO_2 through CO_2 capture, there are still some CO left in the H_2 stream. To purify H_2 , such small amount of CO also needs to be removed. Noble metal catalysts, especially gold-based catalysts, have shown high activity for CO oxidation to CO_2 , but are high costs.[21] During past few years, Pfeiffer's research group at UNAM found that some CO_2 sorbents also can be served as catalysts to convert CO to CO_2 which can be further captured with the same sorbent.[22-27] The first explored sorbent expresses such dual-functionality is Li_2CuO_2 . [22, 26] Fig. 4(a) shows the Li_2CuO_2 weight increase when put it into the pure CO, CO_2 and $\text{CO}+\text{O}_2$ gas conditions. As one can see that Li_2CuO_2 can directly capture CO through reaction $\text{Li}_2\text{CuO}_2 + \text{CO} = \text{Li}_2\text{CO}_3 + \text{Cu}$. The experiments did detect the reduced Cu.[26] However, the reaction takes longer time. Once the O_2 was introduced, the Li_2CuO_2 serves as a catalyst for CO oxidation, following the CO_2 capture through $\text{Li}_2\text{CuO}_2 + \text{CO}_2 = \text{Li}_2\text{CO}_3 + \text{CuO}$. Through the calculations of thermodynamic properties, Fig.4(b) shows the calculated relationship of gas pressures versus temperatures. As one can see that introducing O_2 into CO, the Li_2CuO_2 can catalyze CO oxidation to CO_2 and the CO concentration is reduced very low-level.

Except for Li_2CuO_2 , other sorbents, such as NaCoO_2 , [23] Li_2ZrO_3 , [24] Na_2ZrO_3 , [27] $\text{Li}_5\text{FeO}_4/\text{Li}_2\text{FeO}_2$, [25, 28] also expressed such dual-functionalities, which are very useful to purify H_2 stream. As next direction, similar approach may be applied to NO_x and SO_x removal.

4. CONCLUSIONS

The modeling results showed that from given database we can screen out most promising candidate materials for CO_2 capture technology developments. With similar approach, we also can theoretically design new sorbents by mixing solids and doping with other elements. Therefore, although one single material taken in isolation might not be an optimal CO_2 sorbent to fit the particular needs to operate at specific temperature and pressure conditions, by mixing or doping two or more materials to form a new solid, it is possible to synthesize new CO_2 sorbent formulations which can fit the industrial needs. Our results also show that computational modeling can play a decisive role for identifying materials with optimal performance.

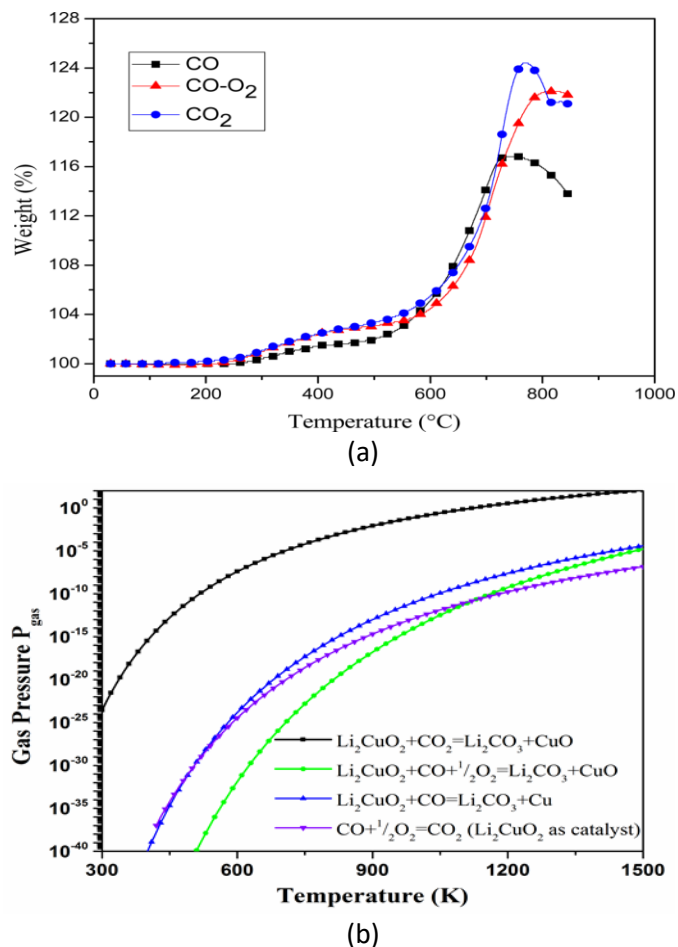


Fig. 4 sorbent Li_2CuO_2 with dual-functionality. (a) experimental measurements of weight increase under CO, CO_2 , $\text{CO}+\text{O}_2$ gas conditions, (b) theoretical calculated gas pressure versus temperature (van't Hoff plot).

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