New Composite Adsorbents for Conversion and Storage of Low Temperature Heat: 
Activity in the Boreskov Institute of Catalysis

Yu. I. Aristov
Boreskov Institute of Catalysis, Prospekt Lavrentieva 5, Novosibirsk 630090, Russia

1. Introduction
The current threat of global changes of the climate, 
due to emission of greenhouse gases [1], bring to the 
fore an increased necessity of rational use of heat. This 
requires new approaches and materials for efficient 
conversion and storage of heat. In this presentation we 
consider, first of all, adsorption methods to 
transforming a huge amount of low temperature heat 
(50-120°C) which now is poorly used and mostly 
dissipated in the ambient in vain. They are adsorptive 
heat storage, heat pumping and cooling. Although these 
three applications are overlapped, each one does 
 impose specific requirements to an adsorbent that is 
 optimal namely for this particular application. 

Attempts to formulate these requirements have been 
done in many papers [2-8]. Here we mainly discuss 
how to synthesise such optimal adsorbent and which 
practical tools are available to do it? This paper is 
directed to summarise the activity of the Boreskov 
Institute of Catalysis, BIC, (Novosibirsk, Russia) on 
synthesis and study of new composite adsorbents of 
water to be used for conversion and storage of low 
temperature heat (sorbent characterisation was partially 
done in co-operation with the ITAE/CNR, Italy).

2. The concept of composite adsorbents
Results of [2-8] clearly showed that for each of the 
three mentioned applications quite different adsorbents 
are required to provide the best performance. Moreover, 
even for fixed application (e.g., an adsorptive cooling), 
in various climatic zones optimal adsorbents should 
significantly differ. Typical cycle of adsorptive chiller 
is displayed in Fig. 1; its description can be found in 
[2-4]. The cycle is determined by the evaporator 
temperature Te, condenser temperature Tc and maximal 
desorption temperature T3. In any case the temperature 
of an external heat source which drives the cycle has to 
be higher than T2. This threshold temperature can be 
estimated from the Trouton’s rule (the intersection of 
vapor pressure lines for T approaching infinity [2]) as

\[ T_2 = \frac{T_3^2}{T_e} \]  

Fig. 2 presents as calculated T2 vs Tc for the three 
cooling applications, namely, the deep freezing (Tc = 
-30°C), ice making (Tc = -5°C) and air conditioning (Tc = 10°C). The value of T2 appears to considerably differ 
for various climatic zones and covers the ranges of 
80-156, 47-116 and 30-96°C for the above 
applications (Fig. 2) [8].

One might thus expect that an optimal adsorbent for 
these particular applications and climatic conditions 
should be quite different and, hence, is a subject of 
careful choice or specific synthesis.

This choice can hardly be done among common 
single component adsorbents. Indeed, although there 
are many trade marks of adsorbents, only few types of 
commercially available materials are known and 
popular among thermal engineers. The majority of 
literature data concern few working pairs, namely, "water – zeolite", "water – silica gel" 
and "methanol – activated carbon" [10, 11]. Many 
types of zeolites are commercially produced, but just
two of them are commonly studied for adsorption cooling, 4A and 13X, probably because they are large-scale products and, hence, they are easily available, well-characterized and cheap. Similar situation exists with silica gels: mainly high density silicas have been tested for heat conversion, like Fuji types A and RD [12, 13], Davison gel types 125 and 127 (Grace and Co.) [14], Spexchem (France), KSMG (Russia) [6], etc. For all these materials the pore diameter \( d \) is 2.0-3.5 nm, the pore volume \( V_p \) is 0.3-0.4 \( \text{cm}^3/\text{g} \) and the specific surface area \( S_{sp} \) is 400-700 \( \text{m}^2/\text{g} \). Another famous type of silica is that of regular density [15] with \( d = 10-15 \text{ nm} \), \( V_p = 0.7-1.2 \text{ cm}^3/\text{g} \) and \( S_{sp} = 250-450 \text{ m}^2/\text{g} \). Sorption properties of these two types are different and represent two boundary situations. The properties of other silicas are more or less between them because the synthesis technologies allow a change in the sorption properties within a relatively narrow range. The high density silica adsorbs more water than the silica with regular density and larger pores, and the difference can reach the factor of 2. Thus, for a single component adsorbent tools to vary sorption properties are rather restricted. Commonly, it is possible to change only the chemical nature of adsorbent and the size of its pores. Sometimes its crystalline structure can also influence sorption properties (for \( \text{Al}_2\text{O}_3 \), \( \text{TiO}_2 \), etc).

Figure 3. Scheme of water sorption on SWSs.

For a two-component adsorbent like "a porous host matrix modified by an active substance" at least two new parameters appear: the chemical nature of the modifying agent and its content, that can open new opportunities in varying and designing sorption properties of the composite. First substances used as the modifying agents were hygroscopic inorganic salts. Since 1929 composite \( \text{CaCl}_2 \) in porous alumina was patented as a dehydrating material [16]. Then, other two-component composites have been proposed for this application, and composite \( \text{CaCl}_2 \) in porous carbon was used in mask-gas. However, no comprehensive study was done to learn properties of the composites because the goal of those studies was technologically focused and restricted to the particular conditions of gas drying. Anyway, it became clear that the modification of common adsorbents by hygroscopic salts can give a tool for managing their sorption properties. This idea was then almost forgotten.

Recently, a new impact has come from the material science to promote this concept. It was originated from a basic research of ultrasubmersed solids and was aimed to answer the question “How do sorption properties of a salt change when it is dispersed inside a porous host matrix?” and “Which factors do influence these changes?” The answer required systematic study, that has been undertaken and resulted in a number of publications on the new family of composite adsorbents "a hygroscopic salt confined to a porous host matrix” synthesised at the Boreskov Institute of Catalysis [17-29]. These materials were called Selective Water Sorbents (SWSs) [18-20]. Now similar adsorbents are being synthesised and studied in many other research centres [30-38]. The SWSs are considered as promising for energy storage [5, 39], heat pumping [40] and cooling [30, 37, 41, 42], because they take an intermediate position between salt hydrates and solid adsorbents and, thus, can combine advantages of both these materials. Indeed, a pure salt can hardly be directly used, because of its corrosive properties, strong swelling/expansion during the reaction with water, very slow kinetics and hysteresis of this reaction, etc. [8]. The salt confinement to pores allows overcoming these obstacles and easy management of composite sorption properties to fit demands of given application, as it will be considered below.

3. Selective Water Sorbents: design of sorption properties

In this Section we review the results on SWSs obtained so far and try to answer the following question: “Which tools has material science to design a composite adsorbent with predetermined properties optimal for particular application in energy sector?”

Here we summarise the activity of the Boreskov Institute of Catalysis in the synthesis of SWSs. So far, more than 40 new sorbents based on halides (\( \text{CaCl}_2 \), \( \text{LiBr} \), \( \text{LiCl} \), \( \text{MgCl}_2 \)), sulphates (\( \text{Na}_2\text{SO}_4 \), \( \text{MgSO}_4 \), \( \text{CuSO}_4 \)) and nitrates (\( \text{Ca(NO}_3)_2 \), \( \text{LiNO}_3 \), \( \text{Mg(NO}_3)_2 \)) of metals incorporated into hydrophilic (silica gels, alumina, clays) or hydrophobic (porous carbons) matrices have been synthesised and studied. After that peculiarities of reversible reaction

\[ <S> + n \text{H}_2\text{O} \leftrightarrow <S \cdot n\text{H}_2\text{O}> \]

between a confined salt \( S \) and water were studied. The reaction results in the formation of the hydrated salt \( <S \cdot n\text{H}_2\text{O}> \). The results of the study were presented in
more than 40 papers, 50 abstracts and 8 patents and have been summarized in [8, 26-28].

Figure 4. Isobars of water sorption by silica gel (pore size 12 nm) (1), by bulk Ca(NO₃)₂ (2), their linear superposition (3) and isobar for composite Ca(NO₃)₂/silica (4) [29]. P(H₂O) = 17 mbar.

The main findings can be generalized as follows:
- three mechanisms of water sorption have been found: a) adsorption by the host matrix, b) chemical reaction between water and salt resulting in the formation of crystalline hydrates, and c) absorption by the salt aqueous solution in the pores (Fig. 3);
- sorption by composite is not a linear combination of that of the host matrix and salt (Fig. 4);
- the matrix can accommodate the salt swelling caused by a chemical reaction between the salt and water;
- gas-solid reaction is much faster for a confined salt than for a bulk one, so that the rate of sorption process is commonly controlled by inter- or intrapartical diffusion;
- inside pores, the synthesis-decomposition hysteresis can be reduced or even avoided (see below).

Moreover, a host matrix provides a network for efficient transfer of heat and reagent which greatly enhances these processes, as it was conceived and reached for composite sorbents of ammonia "salt + expanded graphite" [43] or "salt + carboneous textile Busofit" [44].

The data obtained so far are a fundamental to answer the question “Which practical tools are available to design the optimal adsorbent?” First, we shall list these tools and then give examples of how do they affect sorption properties of a composite “salt in porous matrix”. In our previous studies [18-29, 45-49] it has been clearly shown that sorption properties of SWSs can be peculiarly changed in a wide range by varying
- chemical nature of confined salt,
- average size of pores of the host matrix,
- salt content,
- synthesis conditions.

3.1 Effect of the chemical nature of the confined salt
Since the active substance in SWSs is an inorganic salt, its chemical nature is of prime importance. Fortunately, a plenty of salts can form crystalline hydrates according to reaction (2).

Table 1. Relative pressure ɳ₁ corresponding to various transitions between different salt hydrates, both bulk and confined to silica pores of 15 nm in size.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Transition</th>
<th>ɳ₁ (bulk)</th>
<th>ɳ₁ (confined)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂SO₄</td>
<td>1 ⇒ 7</td>
<td>0.80</td>
<td>0.5 – 0.6</td>
</tr>
<tr>
<td></td>
<td>7 ⇒ 10</td>
<td>0.91</td>
<td>-</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>0 ⇒ 2</td>
<td>0.37-0.39</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2 ⇒ 7</td>
<td>0.52-0.57</td>
<td>-</td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>0 ⇒ 2</td>
<td>0.21-0.23</td>
<td>0.15 – 0.19</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>0 ⇒ 1</td>
<td>0.03</td>
<td>0.001-0.003</td>
</tr>
<tr>
<td></td>
<td>1 ⇒ 2</td>
<td>0.05-0.06</td>
<td>0.003-0.01</td>
</tr>
<tr>
<td></td>
<td>2 ⇒ 4</td>
<td>0.15-0.17</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>4 ⇒ 6</td>
<td>0.24-0.30</td>
<td>-</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0 ⇒ 1/3</td>
<td>&lt; 0.01</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1/3 ⇒ 2</td>
<td>0.04-0.05</td>
<td>0.03-0.04</td>
</tr>
<tr>
<td></td>
<td>2 ⇒ 4</td>
<td>0.16-0.18</td>
<td>0.12-0.14</td>
</tr>
<tr>
<td>LiBr</td>
<td>0 ⇒ 1</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>1 ⇒ 2</td>
<td>0.04-0.05</td>
<td>0.02-0.03</td>
</tr>
<tr>
<td>LiCl</td>
<td>0 ⇒ 1</td>
<td>0.09-0.12</td>
<td>0.04-0.05</td>
</tr>
<tr>
<td></td>
<td>1 ⇒ 2</td>
<td>0.12-0.13</td>
<td>0.06-0.09</td>
</tr>
</tbody>
</table>

Table 1 demonstrates that reaction (2) for various hydrated salts in bulk does occur at values of P/P₉ distributed over a wide range of 0.01 to 0.91. Thus, the first step of salt selection should be the calculation of relative pressure ɳ₁ which corresponds to point 2 of the cycle diagram (Fig. 1) and searching the salt hydrate decomposed at ɳ₁ equal or close to ɳ₁. Then, the chosen salt can be placed inside pores of a host matrix.

3.2 Effect of the pore size of the host matrix
Table 1 also shows that the transition humidity ɳ for confined hydrate can significantly differ from that in bulk. Thus, confining salt to small pores can result in shifting the equilibrium of hydrate formation towards lower relative pressure (higher temperature), what gives a valuable tool for adjusting the transition temperature.

This effect was comprehensively studied by confining Ca(NO₃)₂ to silica with different pore size [29]. A gradual shift was found for the transition between anhydrous salt and its dihydrate (synthesis reaction) from 45-48°C for bulk salt to 53-58°C and 83-105°C for the salt confined, respectively, to pore of
12 and 3.5 nm in size (Fig. 5). Confining the salt inside the pores of silica also reduces the sorption/desorption hysteresis which becomes almost negligible for 3.5 nm pores (Fig. 5).

Figure 5. Isobars of sorption/desorption for Ca(NO₃)₂: bulk (■), confined to pores of 12 nm (Δ/○) and 3.5 nm (▲/●) [29].

3.3 Effect of the salt content

The salt content can affect both the final water uptake and the reaction temperature (Fig. 6) [24].

Figure 6. Temperature independent curves for CaCl₂/ SiO₂ with the salt content 22.3 (▲) and 33.4 % (■).

It was found that reducing the salt content from 33.4 to 22.3 wt.% shifts the transitions (0.33 ⇒ 2) and (2 ⇒ 4) to lower relative pressure (Fig. 6). This effect is caused either by smaller size of salt nano-crystallites deposited on the silica surface from less concentrated salt solution or by the salt-silica interaction [45-47].

3.4 Effect of the synthesis conditions

We have found that among conditions, which can be varied during synthesis procedure the most important are pH of the impregnating solution [46, 47] and calcination temperature [45]. The increase of pH and Tcalc leads to qualitatively similar impacts: the transition becomes less sharp and proceeds over wider range of the relative pressure. This can be explained by the ion exchange interaction between the silica surface and the salt solution, which occurs during the impregnation procedure [45-47]. This interaction was found to cause the formation of the surface complexes Si—O—Ca²⁺—Cl⁻, which stabilizes two phases of the confined salt, namely, the volume crystalline phase and the surface X-ray amorphous phase. The fractions of the crystalline and amorphous phases depend on the salt content and pH of salt solution and affect the sorption equilibrium between the composites and water vapor. Water sorption by the composites, which contain predominantly crystalline salt, leads to the formation of crystalline hydrates of the salt with monovariant equilibrium. Water sorption by the composites, containing predominantly X-ray amorphous phase, monotonically changes with the increase of relative pressure, which is typical for salt solutions and hydrates of the lacunary structure. Relative contributions of the mentioned phases can be also controllably changed by varying the temperature of SWS final treatment [45].

3.5 Adsorbent properties vs. unit performance

Several SWSs synthesised in the Boreskov Institute of Catalysis have already been tested in the ITAE/CNR (Italy) [50, 51]. The adsorber of the chiller was filled with SWS-type material — calcium chloride in silica gel KSK (SWS-1L). The host matrix, active salt and its content (33 wt. %) were selected based on the knowledge gained as described above. The aim was to obtain solid sorbent optimal for air conditioning cycle (Tev = 10°C, Tcond = 35°C) driven by low temperature heat. The tests showed that the cooling COP can achieve 0.6 at desorption temperature as low 85-95°C [50]. This was a gross COP that is affected by heat losses, the heat capacity of the inert masses and the heat efficiency of exchangers, which will be optimised in the next unit. Of course, it can be further improved in a multi-bed system with internal heat recovery. So large COP achieved for a simple unit configuration shows the advantage of this new composite sorbent with respect to common commercial materials (zeolite or silica gel) at such a low regeneration temperature. Indeed, 85-90 °C can be easily obtained with a simple and cheap flat receiver of solar energy or from industrial waste heat. Another prototype has been tested with consolidated SWS layer [51].

Despite encouraging results of the laboratory investigations, only further strict testing of SWSs in real prototypes of adsorptive heat transformers can prove the worth of these new materials.

4. Kinetics of water sorption on SWSs

So far, we considered only equilibrium sorption properties of new composite adsorbents and showed that they can be regulated in a wide range during synthesis stage. For heat pumps or cooling machines with short cycle times dynamical properties like the specific power, become important, too. That is why we
have measured isothermal kinetics of water sorption on loose grains of SWS-1L at T = 33 – 69 °C and P(H2O) = 8 – 70 mbar for various grain sizes Rp (0.355 - 1.4 mm) [52]. For comparison we also measured the same kinetics on loose grains of well-known adsorbent – silica Fuji Davison RD [12, 13]. It was indicated as the adsorbent of water used in Japanese commercialized adsorption chillers which utilize low-temperature heat (50-80°C) [53, 54].

It is appeared, that kinetic behavior of both materials conforms well with the Fickian diffusion model [52, 55] rather than with the Linear Driving Force (LDF) model (Fig. 7) that is often used for modeling adsorptive heat pumps and chillers [56]:
- the dependence of the water uptake on \( \sqrt{t} \) is linear at short times (Fig. 7);
- the apparent water diffusivity depends on the local slope of the water sorption isotherm;
- the Knudsen mechanism of the interparticle diffusion is found;
- contribution of thermal effects for water sorption became significant for small grains.

The pore diffusivity of water in SWS-1L was calculated from experimental data over temperature range 33-69°C \( D_e = (1.2 \pm 0.6) \times 10^{-6} \) m²/s, that is 2-4 times lower than that of the pure silica KSK. The possible reason might be related to a partial blockage of the silica pores by the salt. It could result in the increase of the pore tortuosity and, thus, in the reduction of the effective pore diffusivity. Despite of this difference in the \( D_e \), the specific cooling power \( W = (m_1/m_0) \Delta H_{eq}/t \) generated at the beginning of sorption is the same for both the materials, as the initial slopes are equal (Fig. 7). This is due to the fact that for SWS-1L, the lower diffusivity is compensated by larger equilibrium uptake (Fig. 7), which also leads to higher COP than for the pure silica [52, 55].

The obtained results evidence that for layer of loose grains of the both adsorbants rather short adsorption times can be realized. This could result in the average cooling power 500-1000 W/kg, that makes it possible construction of quite compact adsorptive units for heat transformation.

5. Other SWS-type materials

Composite materials for sorption of ammonia [43, 44, 57-62] and methanol [63-66] have also been developed and tested taking in mind application for heat conversion.

5.1 Ammonia

Recent study of CaCl₂ and BaCl₂ inserted to inorganic matrices [62] confirmed that the ability of the confined salt to absorb NH₃ can differ from those of a bulk salt:
- transitions between complexes CaCl₂\~nNH₃ are shifted to higher ammonia pressure in comparison with those in bulk;
- both the enthalpy and entropy of complex formation for the confined salt are significantly reduced respect to those for the bulk one;
- the equilibrium of ammonia sorption in the confined state is divariant that means the NH₃ uptake increases continuously as the NH₃ pressure rises;
- the solid compound CaCl₂\~8NH₃ does not form inside pores. This could be caused by the formation of a CaCl₂/ammonia solution inside the pores.

5.2 Methanol

A new family of methanol sorbents “salt in mesoporous silica” for utilization in adsorptive air conditioner driven by solar energy or low temperature waste heat (T=65-100°C) has been proposed in the BIC [63-66]. The composites were synthesized by impregnation of various silica gels with an aqueous solution of different salts (CaCl₂, LiCl, LiBr, MgCl₂, NiBr₂, Ca(NO₃)₂, MnCl₂, CuCl₂, CoCl₂, MgBr₂, BaCl₂, CaBr₂). The methanol sorption capacity of composites, under conditions of typical cooling cycle, was measured by using a new express method [64, 65]. Furthermore, estimation of the cooling COP was carried out in order to compare the performance of such sorbents with other methanol, ammonia and water sorbents. Results obtained showed that most of the composites synthesised present methanol sorption ability which is higher than that of common methanol sorbents (e.g. active carbons). The composite LiCl(30.6 wt.%)/SiO₂ appears to show the highest sorption capacity \( w_{ads} = 0.8 \) g/g. Methanol uptake after desorption stage decreases as well \( w_{des} = 0.09 \) g/g giving an uptake variation per cycle \( dw = 0.71 \) g/g. The corresponding cooling COP is 0.74 (maximum \( T_{des} = 363 \) K, single-bed cycle), which is comparable to
the typical COP values of the best water sorbents.

6. Other Applications
Two other applications of SWSs have been realized commercially in Russia. They are a) adsorptive drying of a compressed air that was implemented in twelve oil refinery plants and cryogenic stations in Russia (more than 200 tonnes of SWS-1A are in use) [67] and b) thermal protection of electronic memory chips ("black box") [68]. Other possible applications of SWSs for obtaining water from air [69], desiccant rotary wheels [38], regeneration of heat and moisture in ventilation systems [70] are under intensive investigation.

7. Conclusions
In this communication we give the review of activity developed at the Boreskov Institute of Catalysis of the Russian Academy of Sciences (Novosibirsk) on synthesis and characterization of new composite materials which can be used for conversion and storage of low temperature heat. We mainly focus on how to design new solid sorbents with sorption properties close or even equal to those perfectly fitting particular cycle of heat transformation. It has been concluded that such sorbents should be two-component materials "hygroscopic salt confined to porous host matrix" (called Selective Water Sorbents, SWSs). More than forty SWS composites were synthesized and studied. It was proved that sorption properties of SWSs can be monitored by a proper choice of the chemical nature and content of the confined salt, the average size of pores of the host matrix and synthesis conditions. All these tools can be used to adjust the real adsorbent to the ideal one which was predetermined as an optimal for chosen cycle. Thus, we review the current state-of-the art at the BIC on the new family of the SWS composites.

It is important to mention that although we have mainly considered here water as a refrigerant, new efficient composites of the SWS-type have also been prepared for sorbing ammonia and methanol, thus, confirming the general approach which we are using for synthesis new sorbents.

8. Acknowledgements
The author thanks the INTAS (grant 03-51-6260) and the RFBR (grants 04-02-81028, 05-02-16953 and 05-08-50223) for partial financial support.

References
[20] L. G. Gordeeva et al., Selective water sorbents for...
[52] Yu. I. Aristov et al., Kinetics of water sorption on SWS-1L (calcium chloride confined to mesoporous silica gel): Influence of grain size and


