

# Advances in gelled-electrolyte technology for valve-regulated lead-acid batteries

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## Abstract

In recent years, the valve-regulated lead-acid (VRLA) battery has been developed into a versatile and extremely reliable energy-storage device. When given a correctly specified battery design technology for the required product application, the VRLA battery will offer the end-user, some, if not all, of the following characteristics: high current capability; good reliability under cyclic, deep-discharge conditions (cycle life); good power density; high recharge efficiency; rapid rechargeability; resistant to overcharge; good charge stability (resistant to thermal runaway); no addition of water (topping-up) during service life (maintenance-free); long service life; wide operating temperature; robust design; low cost per Wh; high volumetric energy density (Wh/l); low self-discharge; high gravimetric energy density (Wh kg<sup>-1</sup>); may be stored and used in any position (orientation); resistant to shock and vibration; no need to be recharged immediately after discharge and environmentally 'safe'. The most commonly used gelling agent, fumed silica, has many disadvantages such as, contamination of the local working environment, particularly during paste-mixing, and occupational hygiene and handling problems. It is also bulky to transport and has long gel times unless used at very high concentrations. There is, therefore, an increasing demand for an alternative gelling agent for sulfuric acid in the production of gelled-electrolyte (GEL) VRLA batteries. Silica sols can provide a solution to all of these problems, and moreover at a lower cost to the battery producer. © 2002 Published by Elsevier Science B.V.

**Keywords:** Gel electrolyte; Silica sols; Valve-regulated lead-acid (VRLA) batteries

## 1. Fundamentals of VRLA battery technology

There are two, distinctly different, product technology concepts for immobilizing the electrolyte within the cells of valve-regulated lead-acid (VRLA) batteries which are in commercial production today, namely:

- AGM (absorptive glass-mat) separators, or to apply a more recent terminology, recombinant-battery separator media (RBSM) [1] and
- GEL (thixotropic, micron or sub-micron diameter silicon dioxide, gelled-electrolyte).

Such and batteries are characterized by a severe shortage of electrolyte, which is held, immobilized, within the

'sealed' cell (VRLA batteries are 'sealed' by means of pressure-release valves). The units cannot be opened to add water, which leads to the often misused term of 'maintenance-free'. In addition, they utilize non-antimonial lead alloys for the grids in order to achieve hydrogen overpotentials and thus minimize electrolysis (water loss) during recharge.

The VRLA design results in a much lower battery capacity when compared with traditional, flooded (excess) electrolyte, counterparts. A typical mass-distribution analysis for a 12 V, 84 Ah (20 h rate), GEL-VRLA battery for use in photovoltaic (PV or solar) energy-storage systems is given in Fig. 1 and Table 1, and is compared with that for an alternative 12 V, 94 Ah (20 h rate) flooded-electrolyte battery of similar physical size and weight [2]. The various components are as follows.

### 1.1. Positive grid

A lattice structure manufactured either from lead-antimony alloys for 'deep-discharge cycle' batteries (which require regular periodic additions of water for 'topping-up'),

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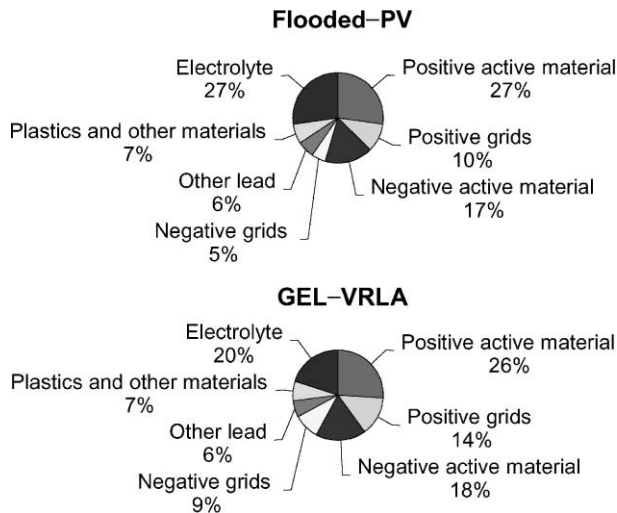


Fig. 1. Comparison of mass distribution of flooded-electrolyte and gel-electrolyte lead-acid batteries for use in solar (PV) energy-storage systems [2].

or from pure-lead, lead–calcium or lead–calcium–tin alloys for ‘maintenance-free’ and VRLA battery types. The grid material is subjected to stretching stresses with each discharge, and corrosion with each recharge. These features eventually result in failure which is exacerbated by high temperatures.

### 1.2. Positive active-material (PAM)

High surface area, micro-porous lead dioxide ( $\text{PbO}_2$ ) which is converted to lead sulfate ( $\text{PbSO}_4$ ) during discharge. The structure of the  $\text{PbO}_2$  is gradually destroyed with each discharge–charge cycle. Eventually, the PAM loses electrical contact with the supporting grid and its ‘capacity’ is lost.

### 1.3. Negative grid

A lattice structure manufactured from lead–antimony or lead–calcium alloys. The grid plays no part in the determination of the cycle-life of the battery, but serves only as a conductor of electrical energy from the negative active-material.

### 1.4. Negative active-material (NAM)

High surface area, micro-porous lead (Pb) which is also converted to lead sulfate ( $\text{PbSO}_4$ ) during discharge. Unlike the PAM, the NAM also contains a small quantity of additives which ensure that the porous structure is preserved

during the life of the battery. These additives, however, are destroyed at high operating temperatures (above 50–60 °C) and this, in turn, can result in premature loss of battery capacity.

### 1.5. Other lead

Lead used in the battery to form the internal (i.e. between each 2 V cell) and external current-carrying connections.

### 1.6. Plastics and other materials

These comprise the case, cover components, etc.

### 1.7. Electrolyte

A dilute solution (typically ~35 wt.%, when fully charged) of sulfuric acid in water that provides the source of sulfate ( $\text{SO}_4^{2-}$ ) ions for the PAM and NAM discharge reactions. Water is gradually lost during each recharge, and in the case of ‘low maintenance’ and ‘deep cycle’ batteries must be replenished periodically. Batteries which use lead–calcium grids still lose water, but at a much lower rate which is usually beyond the expected operating life of the battery.

## 2. GEL–VRLA batteries

Much research and development work has been done, during the 1990s, to understand and improve the technological knowledge base for VRLA batteries [3–11], and in particular for AGM types. By contrast, there has been comparatively little documented and published work on advancing the design, durability and performance characteristics of the GEL–VRLA battery system since its inception by Jacke [12].

It is generally accepted that GEL–VRLA cells and batteries experience less electrolyte stratification than AGM–VRLA types, especially under deep-discharge cycle applications such as those experienced in remote-area power supply (RAPS) operations [13,14]. Stratification causes a capacity decrease because of electrolyte limitation, and results in accelerated cell failure due to grid corrosion and irreversible degradation of active material in the lower regions (i.e. in the zone of higher-than-normal acid concentration) of the plates.

In GEL–VRLA cells, the recombination reaction takes place by the transportation (diffusion) of gaseous oxygen

Table 1

Commonly available 12 V lead-acid batteries which may be used in a 50 Wh solar home system [2]

| Battery type  | Dimension L × W × H (mm) | Weight (kg) | Capacity (Ah at 20 h rate) |
|---|--------------------------|-------------|----------------------------|
| GEL–VRLA (6 positive + 6 negative = 12 plates/cell)   | 315 × 175 × 228          | 26.0        | 84                         |
| Flooded-PV (8 positive + 7 negative = 15 plates/cell) | 331 × 173 × 238          | 26.2        | 94                         |

from the positive to the negative plate through a network of micro-cracks (or fissures) in the gelled electrolyte. Investigations into the gassing kinetics of VRLA cells under constant-voltage (float) charge regimes have shown that the gas-recombination efficiency in cells with AGM separators becomes stable much earlier than that in cells with gelled electrolyte [15]. This phenomenon may be explained by the time taken for electrolyte in the newly filled GEL–VRLA cell to dry-out partially (i.e. for sufficient water-loss to take place with corresponding shrinkage of the gel), and develop the matrix of cracks which is required for oxygen diffusion to take place. Once the oxygen-recombination cycle is established in a GEL–VRLA cell, however, these cells are known to have significantly lower float currents, with a concomitant decrease in water-loss.

In general, AGM–VRLA batteries are very sensitive to operating temperature such that service lives are reduced at elevated temperatures and unstable thermal runaway can occur. This results in the generation of large quantities of oxygen (which recombines exothermically), an increase in internal resistance, drying-out, swelling of the battery-case and in extreme cases, ‘meltdown’ of the lead components and battery explosion.

AGM–VRLA cells are known to have a low internal resistance (0.3–0.8 m $\Omega$  per 100 Ah at 10 h rate) and consequently, have very good high-rate discharge performance (35–45% of the 10 h capacity is dischargeable in 10 min) [16]. This performance capability makes such batteries ideally suited for use in uninterruptible power supply (UPS) systems. The operational requirements of this application also require the battery to be rapidly recharged to a high state-of-charge, in readiness for the next power outage. Such high-rate recharge regimes are associated with significant internal heating and excessive gas evolution, which, in the case of VRLA batteries, enhances water-loss and subsequent drying-out of the electrolyte.

The heat generated by VRLA cells and batteries during the charge–discharge cycle is directly related to electrochemical polarization effects, ohmic losses, and the oxygen-recombination cycle. As a consequence, temperature rises in VRLA batteries must be carefully managed so as to prevent the ever-increasing charge current and temperature-rise effect, i.e. thermal runaway. AGM–VRLA batteries, as opposed to their GEL–VRLA counterparts, are much more susceptible to this potentially catastrophic phenomenon.

Although their capacity per unit volume is lower than conventional flooded-electrolyte designs, GEL–VRLA batteries can provide a reliable, totally maintenance-free, service lives in many cycling applications, e.g. solar (photovoltaic) and motive-power applications [17–19].

Significantly, GEL–VRLA batteries require less overcharge to reach full state-of-charge. The overcharge can be limited to ~5% (or less) which, in turn, improves the cycling efficiency and minimizes grid corrosion and internal heating. Moreover, gassing is reduced to a level where the oxygen cycle can function efficiently [20].

### 3. Gel chemistry

A ‘gel’ is a contiguous three-dimensional network. Two steps lead to the formation of a gel.

1. A reversible step: aggregation and ‘weak’ hydrogen bonding—the sulfate ion ( $\text{SO}_4^{2-}$ ) can act as a bridge between the positively charged particles of silica ( $\text{SiO}_2$ ) at low pH.
2. An irreversible step: the formation of siloxane ( $\text{Si-O-Si}$ ) bridges between the silica particles which leads to very strong inter-molecular bonding.

In GEL–VRLA cells and batteries, it is the formation of irreversible gels which is of fundamental importance. As with all other chemical reactions, the influence of temperature on the gelling process follows the Arrhenius relationship (i.e. the rate of gelling doubles with every 10 °C rise in temperature). The rate of formation and the ultimate stability of a gel are also strongly dependent on the pH, salt concentration and type, silica content and particle size, and time (Fig. 2).

#### 3.1. Effect of pH

The pH influences the surface charge and zeta potential. The point of zero charge for silica is at about pH = 2. At higher values of pH (>2), the surface is negatively charged due to the presence of ( $-\text{SiO}-$ ) groups on the surface of the silica particle. At lower values of pH (<2), the surface is positively charged as a result of the ionization of silanol groups ( $-\text{SiOH}_2^+$ ). The  $\text{H}^+$  ion also functions as a catalyst in

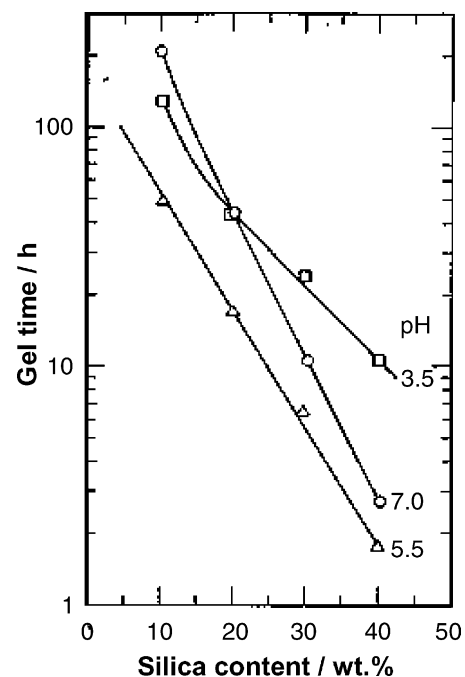


Fig. 2. Gel time vs. silica concentration of 14 nm diameter particles of silica sol at various pH values [21].

the formation of siloxane bonds at pH values below 2, as is the case in sulfuric acid.

### 3.2. Effect of salt concentration and type

A high salt concentration will reduce the zeta potential, and decrease the repulsive interaction (potential energy) between adjacent spherical silica particles which, in turn, increases the strength of the gel. Ions may act as bridges between the silica particles and further facilitate gelling, for example, sulfate ions gel the (positively) charged silica particles at the low pH in a lead-acid battery. Note, sodium sulfate in the region of 1.0–2.5 wt.% may, specifically, be added to the electrolyte in order to aid the recovery of a cell from a very deep discharge, which otherwise may involve a long period of time if the cell is in a fully-discharged state. The sodium sulfate limits the solubility of lead sulfate (the ‘common ion effect’).

### 3.3. Effect of silica content and particle size

The ultimate size of the gelled particles of silica is related to the silica content and their coordination number (i.e. the number of particles touching each other) and this, in turn, will control the pore volume and average pore diameter. As expected, therefore, the higher the silica content, the lower the pore volume and diameter. The effect of silica concentration on gel structure is illustrated in Table 2. Ideally, the silica content of the electrolyte should be as low as possible in order to optimize porosity, yet sufficiently high to develop and maintain a stable gel structure. The particle size exerts a major influence on the pore structure, i.e. large particles give larger pores than small particles. It should also be noted, however, that large particles of low specific surface area result in lower gel strength. Thus, it is important to use a silica sol which has an optimum particle size.

The gelling of  $\sim 5$  M  $\text{H}_2\text{SO}_4$  with silica sols follows the common theory of collision gels, namely, particles will first aggregate and then, with time, form siloxane bonds. At the low pH of the acid electrolyte, the sol will be positively charged, and the sulfate ions will act as bridges between adjacent silica particles and facilitate the processes of aggregation and siloxane bonding. With time, coalescence

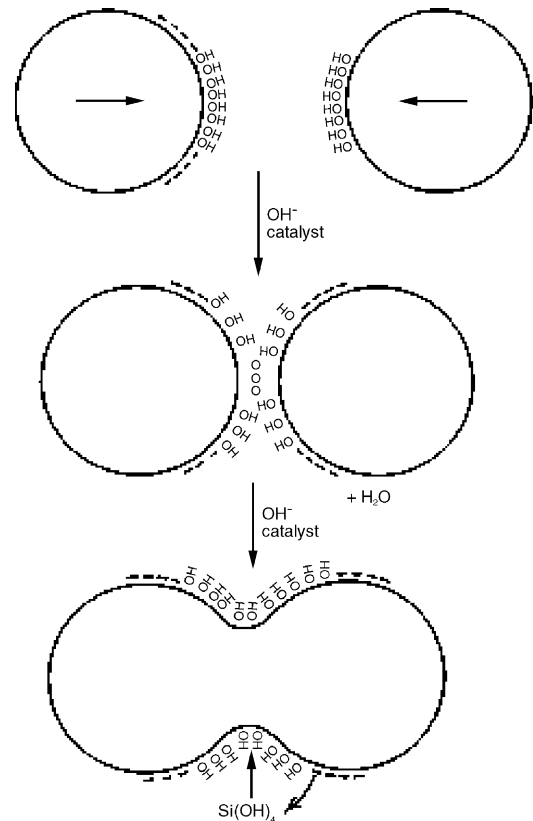


Fig. 3. Illustration of coalescence of gel structure [21].

Table 2  
Gel structure as a function of silica concentration [21]

| Coordination number | Schematic structure | Silica (vol.%) | Gel porosity (%) | Pore volume ( $\text{cm}^3 \text{g}^{-1}$ ) |
|---------------------|---------------------|----------------|------------------|---|
| 6                   |                     | 52             | 48               | 0.4   |
| 3                   |                     | 5              | 95               | 8.4   |
| 3, 2, 3             |                     | 1.3            | 98.7             | 35  |
| 3, 2, 2, 3          |                     | 0.83           | 99.2             | 54  |

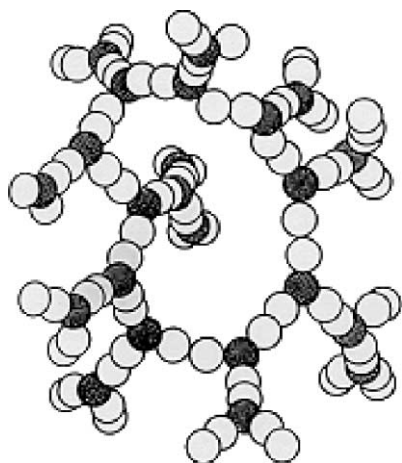


Fig. 4. Packing of spheres with 3, 2, 2, 3 coordination (3: black, 2: white) [21].

(growth) will occur. This is the formation of inter-particle ‘necks by the dissolution and redeposition process rearrangement of silica’ (Fig. 3).

The gel structure from colloidal-silica sols, unlike that from fumed silica, is generally accepted to be based on the three-dimensional packing of silica spheres with coordination numbers which depend on the overall silica concentration, for example, 3, 2, 2, 3 (Fig. 4).

#### 4. Polymerized, thixotropic or collision gels

Three variants of silica may be used to produce a gel, namely, water-glass, fumed silica, or colloidal silica sols. Water-glass rapidly produces a polymerized gel structure but has high alkalinity, experiences liquid separation from the gel, and contains significant levels of impurities (such as iron and chloride ions). Consequently, the material is totally unsuitable for use in lead-acid cells.

Gels produced from fumed silica are commonly used and have a higher initial viscosity than silica sol gels (due to their rod-like structure). They act more like a thickener, but have a very open structure. Unfortunately, they may also contain unacceptable amounts of impurities which are detrimental to the life of a lead-acid cell, in particular chloride ions if the fumed silica is produced from the common process of combustion (burning) of silicon chloride ( $\text{SiCl}_4$ ). Furthermore, fumed silica is very expensive (approximately US\$ 9–18 per kg as pure silica), and extremely difficult to handle (due to the light, fluffy, powdery nature of the material) during mixing.

Although less commonly used, silica sols produce collision gels which have several important advantages in the production of gelled electrolyte. They also impart some very beneficial properties to the gel, namely:

- simple handling and storage (low viscosity, liquid silica sol);
- no separation of liquid from the gel;

- optimum gel strength;
- easily controlled gel time;
- high silica concentration in the sol;
- high purity sol with minimal levels of dangerous contaminants (e.g. iron and chloride);
- easily controlled mixing procedures and
- low cost (approximately US\$ 2.60–3.50 per kg as pure silica).

#### 5. Silica sols as gelling agents

The following four different, commercially available, grades of silica sols have been evaluated as potential gelling agents. Each sol has been mixed with 100 g sulfuric acid (98 wt.%) in a total of 265 g of electrolyte to give a final relative density of 1.300 at 20 °C.

1. BINDZIL<sup>®</sup> AG4000 is a colloidal dispersion of discrete, spherical, silica particles (40 wt.%) in weakly alkaline water. These uniform, high surface area ( $220 \text{ m}^2 \text{ g}^{-1}$ ), sub-microscopic particles (diameter 12 nm) consist of pure amorphous silicon dioxide stabilized with a small amount of sodium hydroxide. The extremely low chloride content of this product allows a silica dosage of up to ~15 wt.%  $\text{SiO}_2$  in the total electrolyte weight without exceeding  $5 \text{ mg l}^{-1}$  of chloride in the filling acid, the limit according to the DIN 43 530 standard.
2. BINDZIL<sup>®</sup> AG3000 is a less concentrated (30 wt.%  $\text{SiO}_2$ ) colloidal dispersion of much smaller (diameter 7 nm), very high surface area ( $360 \text{ m}^2 \text{ g}^{-1}$ ), silica particles.
3. BINDZIL<sup>®</sup> AG2000 is a concentrated (40 wt.%  $\text{SiO}_2$ ) dispersion of high surface area ( $250 \text{ m}^2 \text{ g}^{-1}$ ), sub-microscopic particles (diameter 11 nm).
4. BINDZIL<sup>®</sup> AG1000 is a less concentrated (30 wt.%  $\text{SiO}_2$ ) dispersion of high surface area ( $290 \text{ m}^2 \text{ g}^{-1}$ ), sub-microscopic particles (diameter 9 nm).

The following parameters have been measured.

1. Gel time: this is the time to form a rigid gel which does not show any surface deformation upon inversion. The gel time ( $T$ ) at the test temperature ( $t$ ) is normalized to 20 °C using the relation:

$$T_{20} = T_t \times 2^{(t-20)/10} \quad (1)$$

2. Gel strength: this is measured, 24 h after mixing, as the penetration depth of a lead sphere (weight 0.5 g) when dropped from a height of 23 cm above the surface of the gel. An acceptable gel is defined to have a penetration depth of between 2 and 3 mm.
3. Remaining gel strength: the gel is redispersed at high shear by a dissolver turbine at 1200 rpm for 30 s, and the gel strength is again measured (as above) after a further period of 24 h.

<sup>3</sup> BINDZIL<sup>®</sup> is a registered name of EKA Chemicals AB.

**6. Results and discussion**

An acceptable gel strength can be produced from mixtures containing either ~7.0 wt.% BINDZIL® AG1000, ~7.6 wt.% BINDZIL® AG3000, ~9.0 wt.% BINDZIL® AG4000, or ~11.5 wt.% BINDZIL® AG2000 (Fig. 5).

Ideally, the gel time must be sufficiently long to facilitate mixing and to ensure that the electrolyte can penetrate into all the voids of the cell during filling before it starts to solidify. The resulting gel should also contain a minimum amount of silica (silica has a density of ~2.2 g cm<sup>-3</sup>) both for reasons of cost and more importantly, to maximize the amount of sulfuric acid (the third active material) in the electrolyte contained within the cell.

BINDZIL® AG1000 has the shortest range of gel times in relation to the silica content (concentration) in the final electrolyte. BINDZIL® AG3000, and BINDZIL® AG2000 display similar gel-time to silica-content relationships (Fig. 6). BINDZIL® AG4000 requires the longest time. Of importance to the battery technologist is the gel time

Table 3

Comparison of silica dosage and gel time required to give optimum gel strength for commercially available grades of silica sols

| Colloidal silica (grade) | Silica dosage (SiO <sub>2</sub> wt.%) | Product dosage (wt.%) | Gel time at 20 °C (min) |
|--------------------------|---------------------------------------|-----------------------|-------------------------|
| BINDZIL® AG1000          | 7                                     | 23                    | 46                      |
| BINDZIL® AG2000          | 11                                    | 28                    | 25                      |
| BINDZIL® AG3000          | 8                                     | 27                    | 80                      |
| BINDZIL® AG4000          | 9                                     | 22                    | 79                      |

at the silica content which is required to give the optimum gel strength, namely, a penetration depth of 2 mm. The results are summarized in Table 3.

**7. Conclusions**

Gelled electrolytes which are based on a mixture of silica sols and sulfuric acid (so-called, collision gels) may realize

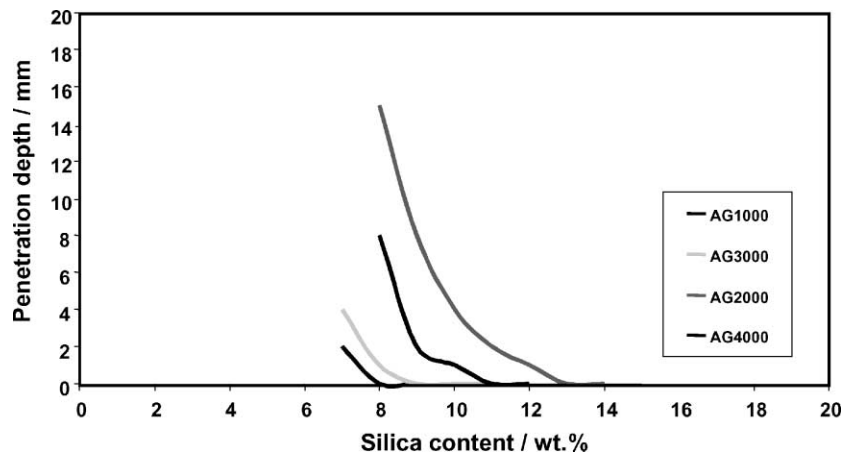


Fig. 5. Comparison of gel strength vs. silica content (pure SiO<sub>2</sub> wt.%) for commercially available grades of silica sols in 1.300 relative density sulfuric acid.

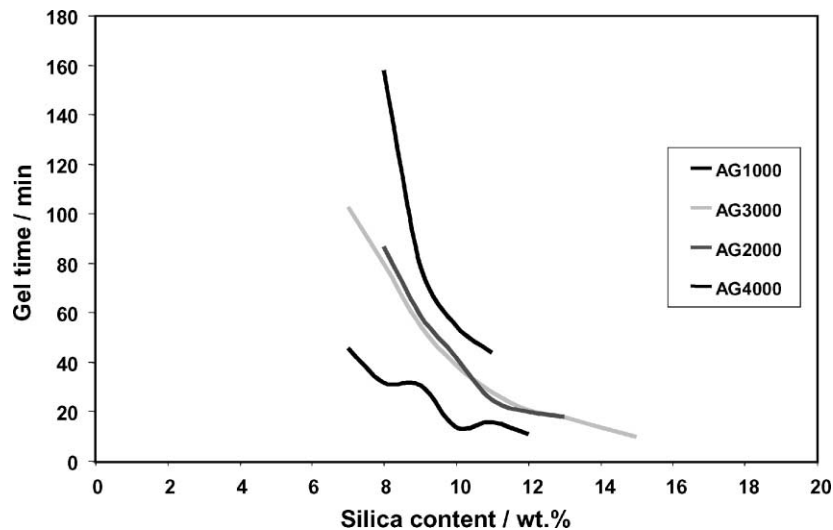


Fig. 6. Comparison of gel time vs. silica content (pure SiO<sub>2</sub> wt.%) for silica sols used to produce the data given in Fig. 5.

the following beneficial technological properties in VRLA batteries:

- simplified handling and mixing of the liquid silica sol;
- no liquid separation from the GEL after ‘setting’;
- improved gel strength from a lower silica content;
- controlled gelling time;
- increased residual gel strength;
- high silica concentration in gelling additive;
- reduced levels of impurities detrimental to the life of a VRLA cell and
- lower cost.

The family of silica sols known commercially as BINDZIL<sup>®</sup> AG1000, BINDZIL<sup>®</sup> AG2000, BINDZIL<sup>®</sup> AG3000 and BINDZIL<sup>®</sup> AG4000 offer the battery designer the ability to tailor precisely the characteristics of the gelled electrolyte, in particular, gel strength, gel time and silica content. These sols have different, uniform particle sizes and surface areas, which confer different properties of gelling time and ultimate gel strength on the gelled electrolyte. Thereby, the sols facilitate the optimization of the performance of the electrolyte in GEL–VRLA cells (for different GEL–VRLA battery applications).

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