SYNGAS CLEAN-UP SYSTEM KINETICS INVESTIGATION

by

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Zinc oxide and hydrogen sulfide reaction was researched experimentally. Dynamic characteristics (solid phase mass change per time, temperature change per time inside the reactor, gas volume flow rate on inlet) were obtained for pure ZnO powder and granular sorbent Katalco 32-4-Johnson & Matthey by thermogravimetric analyzer. Pre-exponential factor, energy activation and specific mass flow rate of ZnO were numerically calculated for pure ZnO. Pure ZnO, ZnO_2SC, and granular sorbent conversion rates were compared. Thermogravimetric experiments with pure ZnO and with ZnO_2SC were simulated in ANSYS Fluent software. Kinetic constants were input parameters for CFD software. Simulation data and experimental results agree well on sorbent conversion diagram.

Key words: *syngas, hot dry desulfurization, kinetics, zinc oxide, CFD*

Introduction

The integrated gasification combined cycle (IGCC) technology is one of the promising directions in coal elaboration field. Sustainable and trouble-free operation of such systems is impossible without reliable and energy-efficient syngas desulphurization units. To date, there are two main types of desulfurization systems: cold wet and hot dry.

The cold wet desulfurization includes technologies based on methyl ethanolamine (MEA), diethyl ethanolamine (DEA), and methyldiethanolamine (MDEA) liquid reagents, the reaction processes of hydrogen sulfide with alkali metal hydroxides, the absorption of hydrogen sulfide by potassium carbonate or sodium carbonate, and the so-called processes Rectisol, Amisol, and Sulfinol. Cold wet technology also includes oxidizing processes: Stratford and Lo-Cat process and selective and non-selective desulfurization [1].

Hot dry desulfurization is based on the process of absorption of hydrogen sulfide by solid sorbents. The most promising sorbents are varieties based on metal oxides. One of the known drawbacks of dry desulfurization is the utilization of waste sorbents, which creates economic difficulties in using this type of treatment, as a rule, hot dry desulphurization is used in technological schemes that have a limited hydrogen sulfide content in the gas (no more than 200-500 ppm) [1].

Simulations show an unambiguous advantage of hot desulfurization before cold, which can be seen from tab. 1 [2-8]. Air-blown IGCC processes were compared in [2], air-blown IGCC and oxygen-blown IGCC were compared in [3]. Inlet gas mass-flow rate was 150-260 kg/s at the pressure of 29 bars and temperature 35 °C, depending on the coal type and

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CO_2 clean-up availability. The MDEA was the base of cold wet clean-up. Clean-up efficiency was less than 97%, while mole hydrogen sulfide concentration was 0.07%. Hot dry clean-up system was calculated considering reversible ZnO sorbents. As a result, exergic losses in the air separation unit, in nitrogen compression and mixing systems, in the gas turbine, and in the combustion chamber of the gas turbine, as well as in some other non-basic systems, were higher in oxygen-blown IGCC rather than in air-blown IGCC. However, the exergy losses in the gasifier, in the syngas cooler and clean-up system, in the steam generator and in the steam cycle in the air cycle proved to be higher than for the oxygen cycle, which generally failed to prevent the air gasification cycle from achieving 1.5% higher total net efficiency than the oxygen-blown IGCC shown in tab. 1.

Table 1. Different types of IGCC net efficiency coefficient comparison

Clean-up system	Net efficiency [%]
Cold wet oxygen-blown	45.5
Cold wet air-blown	47.0
Hot dry oxygen-blown	50.0
Hot dry air-blown	51.5

Hydrogen sulfide and MDEA reaction temperature is 50-150 °C. Hot dry desulfurization process temperature usually is 400-650 °C, and higher (for titanium oxide and copper oxide based sorbents). The ZnO based sorbent regeneration temperature is 750 °C. According to researches [4] sorbent regeneration has no afect on total net efficiency. High temperatures conditions of the hot dry clean-up save more thermal energy than it can be obtained in the cold wet system [4-8]. Calculations have defined that total net efficiency of the IGCC with hot clean-up system is higher than total net efficiency coefficient of the IGCC with cold wet clean-up more than 4.5%.

Experimental results are in good agreement with simulations. Nevertheless this new technology needs to be time-tested. Particular attention should be paid to the failed Pinon Pine project, which valuable experience can prevent the recurrence of such errors in the future [9]. Commercial projects related to the use of the hot dry desulphurization are not known to date. Laboratory tests were carried out at the Nakoso station and at the RTI station in City of Tampa, Fla., USA. The RTI testing of hot gas clean-up reached excellent results, probably this technology can show itself best in industrial operation [10-13].

The IGCC technology has proved itself with forge coal gasification [14], this technology uses a hot dry desulphurization system with use of manganese oxide as a sorbent. Manganese oxides are preferable due to their low cost compared to the reversible analogues based on ZnO and aluminum dioxide. According to [15], similar sorbents can be used for metal smelting, thus becoming a dual-use raw material.

Method

One of the simplest and most accessible methods for determining the kinetic parameters of reactions between the sorbent and gas is the method of thermogravimetric analysis, the essence of which is to record the mass change of a solid sample over time under high-temperature reaction with a reactant gas or with a gas mixture.

Figure 1 presents scheme of experimental installation, with the thermogravimetric analyser (TGA) as the main joint. During investigations TGA Netzsch STA 449 F3 Jupiter equipment was used [16, 17]. Allowed range of furnace heating is 0.001-50 K per minute. Inner weight resolution is 1 μg. Standard TG holder with S-type thermocouple was used in experiments.

Due to good regeneration properties and wide application in the industrial desulphurization systems [18, 19], ZnO was used as the experimental sorbent material. There were studied both fine powder (80-100 μm) and granular industrial sorbent (3 mm) with 60-90% ZnO concentration. Reversible ZnO fine powder (80-100 μm) sorbents shown in fig. 2 are used in transport reactors systems [11], while large granular sorbents with particles 3 mm in diameter are used in fixed bed reactors. Since hot desulfurization of the large air-blown IGCC is carried out in transport reactors, special attention was paid to the highly dispersed powder.

The reaction of desulfurization proceeded according to the formula:

$$ZnO + H_2S = ZnS + H_2O \qquad (1)$$

The reaction of a thin layer of a finely dispersed ZnO powder is described by a volumetric model. The process of particle conversion appears to be a one-stage process, in the form of a heterogeneous reaction of hydrogen sulfide absorption by ZnO, resulting in water vapor and ZnS formation. The reaction occurs throughout the volume of the particle and continues until all ZnO is converted to sulfide (ZnS resistance penetrates hydrogen sulfide into the ZnO zone). In large scale installations incidental reactions may occur [20], but they were not taken into account in present study. The equation for reaction rate kinetics is:

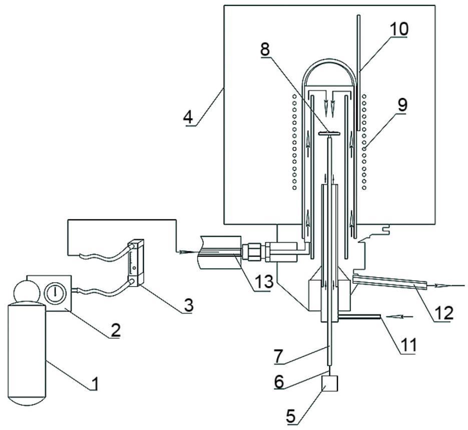


Figure 1. Schematic diagram of thermogravimetric analysis experimental installation; *1 – gas mixture vessel, 2 – reducer, 3 – rotameter, 4 – reactor, 5 – balance, 6 – sample holder, 7 – holder protector, 8 – sample, 9 – electrical heater, 10 – thermocouple, 11 – protection gas inlet, 12 – gas outlet, 13 – raw gas inlet*

$$R_\tau = \frac{1}{m_\tau}\frac{\mathrm{d}m}{\mathrm{d}\tau} = \frac{1}{1-X}\frac{\mathrm{d}X}{\mathrm{d}\tau} = k_{\mathrm{CO}}\exp\left(-\frac{E_a}{\mathrm{R}T}\right) = k_{\mathrm{C}}(T) \qquad (2)$$

Investigations of ZnO kinetics

A gas mixture of 1% hydrogen sulfide and 99% of argon was used. Normal volume flow rate range was 0.2-0.3 nL per minute. Sample holder was filled with pure ZnO fine powder (50-100 μm) with initial mass 17 ± 0.1 mg (room temperature). Studies were carried out in the temperature range from 250 to 950 °C with a heating-rate 20 K per minute shown in fig. 3.

The kinetics of ZnO particles reaction in temperature range m_1-m_2 was described by volumetric model in eq. (2). According to our observations, ZnO particles are aggregated at the room temperature into loose formations with a size of 1 mm. Figure 4 shows that the dependence of the reaction rate from the conversion rate has a dramatically rising character.

Figure 2. Sample holder with pure ZnO

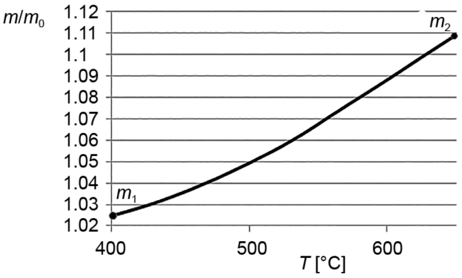


Figure 3. The ZnO sorbent mass growth as a function of temperature

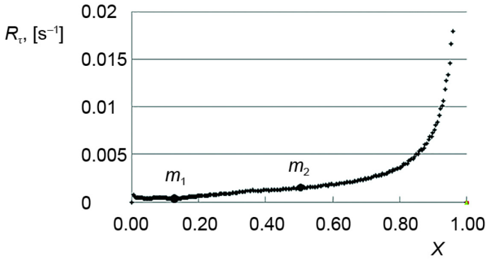


Figure 4. The dependence of the ZnO sorbent reaction rate from the conversion rate

The representation of the temperature dependence of the reaction rate in the Arrhenius plots shown in fig. 5 allows to select a segment (m_1-m_2), where relation of R_τ is described by volumetric mechanism shown in eq. (2).

The pre-exponential factor and the activation energy are determined by linearizing eq. (3). Figure 6 shows the dependence of the reaction rate constant from the temperature:

$$\ln[k_\mathrm{C}(T)] = \ln[k_\mathrm{CO}(T)] + \left(-\frac{E_a}{\mathrm{R}}\right)\frac{1}{T} \tag{3}$$

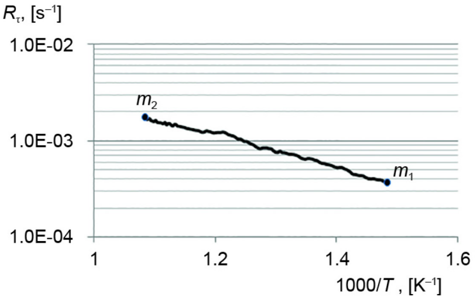


Figure 5. The dependence of the reaction rate of the sorbent ZnO from the inverse temperature

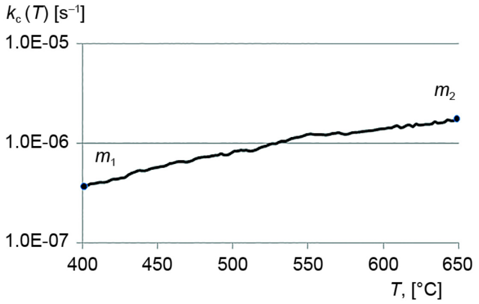


Figure 6. Dependence of the reaction rate constant from the temperature in the reactor

Table 2. The ZnO kinetics constants

Average values in the temperature range 400-650 °C	
E_a, [kJmol^{-1}]	k_CO, [s^{-1}]
32.5	0.00013

Values of the pre-exponential factor and the activation energy are given in tab. 2.

Granular sorbent dynamics investigation

As a sample, the industrial sorbent Katalco 32-4 grade with the density of 2900 kg/m^3 was taken. The chemical composition of the sorbent: 60-90% of pure ZnO, 3-7% of aluminum oxide, 3-7% of calcium oxide. As a sample, a spherical granule of a sorbent 3 mm in diameter and mass 92.55 mg was taken. Argon was supplied to the reactor with a hydrogen sulfide content of 1% in an amount of 0.2 nL per minute, as in the previous experiment. The temperature in the reactor was increased from 250 to 475 °C at the heating rate of 20 K per minute. Figure 7 shows the dependence of the mass increase during heat-up was close to linear in the chosen temperature range.

Figure 8 shows the dependence of the conversion degree on time is also linear in the chosen temperature range.

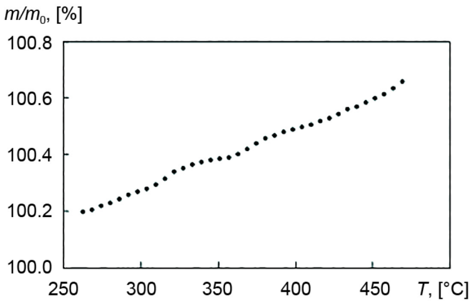


Figure 7. The mass increase of the granular industrial sorbent Katalco 32-4 J & M, depending from the temperature

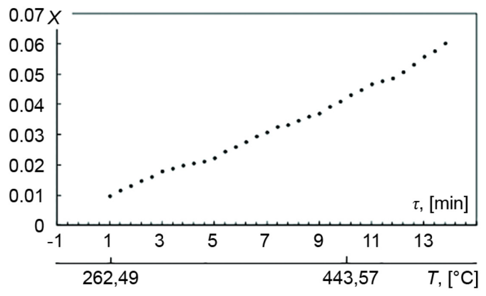


Figure 8. Conversion of granular industrial sorbent Katalco 32-4 J & M per time

The weight gain was 0.86 mg in 14 minutes. The specific mass-flow rate of ZnO for the reaction with hydrogen sulfide is:

$$G^{P}_{\mathrm{ZnO}} = \frac{\Delta m}{60\Delta\tau m_0} = \frac{0.86\cdot10^{-6}}{60\cdot14\cdot92.55\cdot10^{-6}} = 1.11\cdot10^{-5}\ [\mathrm{kgZnO/kgsorbent}\cdot\mathrm{s}] \tag{4}$$

$$G^{P}_{\mathrm{H_2S}} = G^{P}_{\mathrm{ZnO}}\frac{M_{\mathrm{H_2S}}}{M_{\mathrm{ZnO}}} = 1.11\cdot10^{-5}\frac{34}{81} = 4.64\cdot10^{-6}\ [\mathrm{kgZnO/kgsorbent}\cdot\mathrm{s}] \tag{5}$$

where M_{ZnO} [kgmol^{-1}] is the ZnO molar mass, M_{ZnS} [kgmol^{-1}] – the ZnS molar mass.

Modeling the process in reactor of experimental set-up

The calculations were based on the hydrodynamic multiphase Euler model [21-23]. Three components were included in the gaseous phase: argon, hydrogen sulphide, and water vapor. The solid phase contained particles of ZnO and ZnS. The boundary condition for the gas inlet included 1% volume concentration of the hydrogen sulfide in the gaseous phase in a mixture with argon at the temperature of 20 °C. The gas consumption was taken from the experimental data. At the initial time, the solid phase consisted only of ZnO particles with size 50 μ. The heat exchange between the solid and gaseous phase was calculated according to Gunn law [24]. The pre-exponential factor and the activation energy were taken from the results of the experiments. The initial reaction temperature was taken at 300 °C, which also corresponds to the empirical data. Values of the used materials physical properties are shown in tab. 3.

The CFD simulation parameters were the following. The 3-D mesh quality: minimum orthogonal quality was 2.90e-01, maximum aspect ratio: 1.38e+01. Resolution included transient formulation with first order implicit finite difference scheme and pressure-velocity coupling. Gradient was counted by Green-Gauss cell based method. Second order up-wing

Table 3. Simulated materials physical properties

	Unit of measurement	Value
ZnO density	[kgm^{-3}]	5610
ZnS density	[kgm^{-3}]	3940
ZnO thermal conductivity	[Jkg^{-1}K^{-1}]	530
ZnS thermal conductivity	[Jkg^{-1}K^{-1}]	515
ZnO standard state enthalpy	[kJmol^{-1}]	–350
ZnS standard state enthalpy	[kJmol^{-1}]	–201
ZnO standard state entropy	[Jmol^{-1}K^{-1}]	43.5
ZnS standard state entropy	[Jmol^{-1}K^{-1}]	57.70
H_2S density	[kgm^{-3}]	1.36
H_2O density	[kgm^{-3}]	0.39
H_2S heat capacity	[Jkg^{-1}K^{-1}]	34.2
H_2O heat capacity	[Jkg^{-1}K^{-1}]	2040
H_2S standard state enthalpy	[kJmol^{-1}]	–20.15
H_2O standard state enthalpy	[kJmol^{-1}]	–241.84
H_2S standard state entropy	[Jmol^{-1}K^{-1}]	122.2
H_2O standard state entropy	[Jmol^{-1}K^{-1}]	188.74

scheme was used for momentum simulation. Volume fraction, mass fractions of gas and solid components were counted by first order up-wing scheme. Boundary conditions were the following: gas-flow volume rate 0.3 nm per minute; inlet surface was on the top of the grid, pressure outlet was on the bottom surface of the grid.

Results

Contour of the gas velocity is shown in fig. 9. In the upper part of the reactor, above and below the sample and in the closed protective gas line, as expected, the velocities were close to zero. At the inlet and outlet, as well as in the constrictions between the holder and the wall, the flow reached its maximum values at a speed of 2 to 3 mm per second.

The reaction was uniform throughout the sample volume in accordance with the used volume model. Volumes occupied by ZnO and ZnS are equal. However, the mass content over time changed. The mass fraction (mf) of ZnO in the sample dropped to zero when the mass fraction of ZnS increased to unity within 20 minutes, as shown in fig. 10.

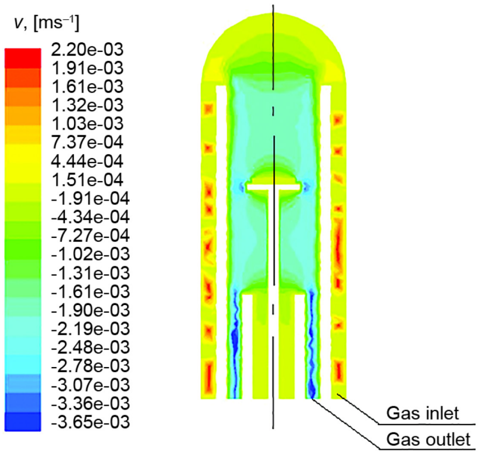


Figure 9. Vertical gas velocity contours
(*for color image see journal web site*)

Figure 11 shows, how water vapor was accumulated on the surface of the solid phase, the concentration of which falls dramatically on gas solid interface boundary.

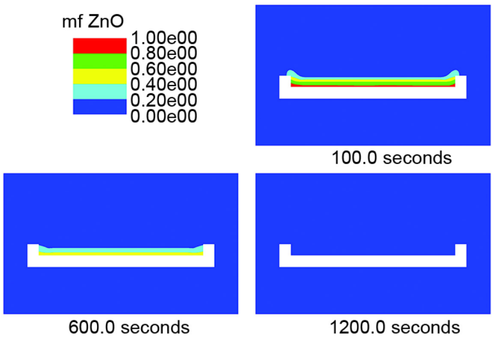
Comparison of different sorbent conversion dynamics is shown in fig. 12. The lines in the figure indicate the experimental data and the points represent the calculated values from the model (2) with the kinetic constants determined in the experiment.

Conversion of powdered sorbent calculations based on ZnO_2SC zinc, studied in [19], were carried out at the constant temperatures of 300, 400, 500, and 600 °C. The particle diameter in the experiments [19] was 90-250 μm, the sample mass 500 mg, the flow rate of the simulator gas 500 ml per minute with a hydrogen sulfide content of 500 ppmv in nitrogen. The calculated points are shown in the graph near curves 3-6.

As can be seen from fig. 12, the rate of conversion of granular industrial sorbent Katalco is almost 20 times lower than the conversion rate of ZnO powder and 2-3 times lower than the conversion rate of fine particles of ZnO_2SC sorbent.

Conclusion

In researches kinetic parameters of interaction of hydrogen sulfide with ZnO and dynamic characteristics of the Katalco sorbent were obtained, comparison of the results with kinetic parameters of other sorbents were also carried out. The rate of conversion of granular Katalco sorbent was almost 20 times lower than the conversion rate of ZnO powder and 2 to 4 times slower than the rate of conversion of the ZnO_2SC sorbent powder. In time range 0-20 minutes average reactor temperatures for lines 1, 2, 3, 4, 5, and 6 were 500 °C (300-700 °C), 350 °C (262-443 °C), 600 °C, 500 °C, 400 °C, and 300 °C, respectively. Sample masses for pure ZnO, ZnO_2SC, and granular sorbent were 17 mg, 500 mg and 92.55 mg respectively. Particle sizes of pure ZnO, ZnO_2SC and granular sorbent were 80-100 μm, 90-250 μm, and 3 mm, respectively. Reaction both in pure ZnO and ZnO_2SC was going in whole the volume, ZnO_2SC has an extremely large surface area 262 m^2/g [19, 25], granular sorbent reaction might occur only on the surface of the sphere according to its pressed consistency. It can be seen, that pure ZnO and ZnO_2SC has close temperatures and close range of diameters, but sample mass of pure ZnO is much less than sample mass of ZnO_2SC, it can be the main reason of dramatic difference between ZnO and ZnO_2SC conversion rate. On the other hand sample mass of granular sorbent is much less than the sample mass of ZnO_2SC (92.55 mg against 500 mg), while temperatures were the same (350 °C against 300 °C). But ZnO_2SC was not granular, and reaction had an ability to occur in whole the volume of the sorbent, while it could not be in Katalco sorbent because of its large size and pressed structure, that couldn't allow gas get inside the sphere.



100.0 seconds
600.0 seconds
1200.0 seconds

Figure 10. Mass fraction (mf) of ZnO in the volume of the solid phase per time
(*for color image see journal web site*)

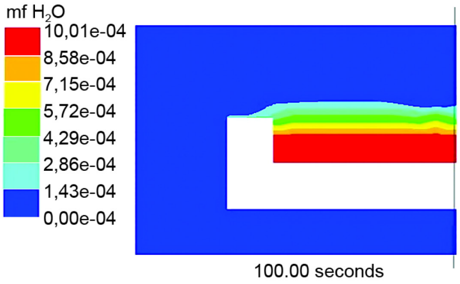


Figure 11. The H_2O mass fraction
(*for color image see journal web site*)

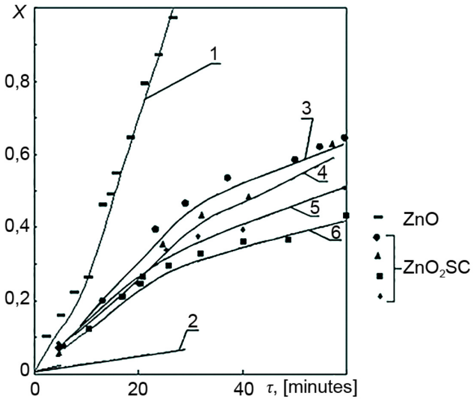


Figure 12. Summary diagram of conversion dynamics of various ZnO sorbents; *1 – ZnO in the temperature range 250-950 °C, 2 – sorbent Katalco in order of temperatures 250-475 °C, (3-6) – powder of ZnO_2SC sorbent according to [19] for isotherms 600, 500, 400, 300 °C. Lines – experiment, markers – calculation*

On the basis of experimental data, computer simulation of the process of hydrogen sulfide absorption by ZnO in the gas stream was carried out. The experimental and modeling results are in good agreement. The model can be used to calculate the operating characteristics of the fluidized bed desulfurization units for IGCC projects.

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Nomenclature

E_a – energy activation, [Jmol^{-1}]
$G^P_{H_2S}$ – H_2S specific mass-flow rate, [kg H_2S/kg sorbent·s]
G^P_{ZnO} – ZnO specific mass-flow rate, [kg H_2S/kg sorbent·s]
k_C – reaction rate constant, [s^{-1}]
k_{CO} – pre-exponential factor, [s^{-1}]
M_{H_2S} – hydrogen sulfide molar mass, [kgmol^{-1}]
M_{ZnO} – ZnO molar mass, [kgmol^{-1}]
m_0 – initial sample weight, [kg]
m_τ – current sample weight, [kg]
Δm – mass increase, [kg]
n_1 – reaction order, [–]
R – gas constant, [m^{2}kgs^{-2}K^{-1}mol^{-1}]
R_τ – reaction rate, [s^{-1}]
T – reaction temperature, [K]
X – conversion rate, [–]

Greek symbol

$\Delta\tau$ – time interval, [s]

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