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Utilization of Kaolin Clay for Enhanced Ballast Water Treatment

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Abstract

Treatment of ballast water from ships using aluminosilicate clay from Ikpeshi, Edo State was studied. The physiochemical parameters and poly-aromatic hydrocarbon content of the water were measured before and after treatment using standard methods. Clay was characterized using x-ray diffractometer and atomic absorption spectrophotometer (AAS). The results of the analysis showed that some parameters of the water as electrical conductivity, 1:309.000, salinity 45.31%, nitrates 7.32 mg/l, phosphorous 4.21 mg/l, total bacterial count 5.8×107cfu were higher than the permissible levels which may be detrimental to the ecosystem. After treatment with kaolin aluminosilicate clay, their levels were reduced. Dissolved oxygen was increased from 2.42 to 6.30 mg/l, while total alkalinity decreased from 25.21 mg/l to 8.110 mg/l, total turbidity from 24.03 to 4.3× 10 mg/l, total dissolved solids from 350 mg/l to 5.23 mg/l and total hardness 37.32 to 4.532 mg/l. The treatment caused reduction in some of the parameters which in turn favour aquatic life forms and improves the ecosystem in general. It is therefore pertinent to conclude that kaolinte clay is a promising adsorbent for the treatment of ballast water in ship both off-shore and on-shore and can effectively remove solids, organic solvents and toxins from ballast water, it is abundant, easy to apply and low-cost.

Keywords: Ballast water, Treatment, Clay, Ship, Adsorbent.

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1.0 INTRODUCTION

Ballast water is seawater taken on hold in a vessel or ship while on board to maintain stability while moving from one shoreline to another within the same or different country (Umudi and Umudi, 2024a). It is usually discharged before loading or unloading. This waters either fresh or seawater in the ballast tank of cargo hold in ship is used to provide stability during loading and unloading. It is a recognized threat to the environment for transportation of invasive marine species into its new environment (Sayinli *et al.*, 2022). This translocation causes changes in ocean and coastal water biodiversity as well as movement of organic and inorganic metals and sediments present in ballast water, thus a critical factor in spreading pollution and demanding ecological balance (GEF-UNDP-IMO, 2010). Seawater is taken into ballast tanks in different compartments on the ship in this case the stability of the ship is corrected. This is called ballast water management.

Pollutants from domestic, agricultural and industrial activities deteriorate the eco-balance and its species. The movement of shipping vessels from one ocean to another introduces non-indigenous organisms (micro and macro), inorganic and organic contaminants through vessels containing ballast water during their voyage (Umudi and Umudi, 2024b). It is globally recognized that ballast water is a threat by introducing invasive species especially in the marine environment (Altug *et al*., 2012; Elçİçek *et al.,* 2023).

Ballast water reduces stress on the hull of ship, improves propulsion, stability, maneuverability and equates the weight loss as a result of loss of fuel/water reduces consumption. At the point of filling the tank, marine organisms, pollutants and sediment are taken along and discharged at their destination into a different environment (alien). In this process there is transfer of organisms that cause destruction ecologically and economically. These invasive non-native species uncontrollably reproduces themselves, transported along ballast water and bottom tanks to other new environments. They dominate it causing ecological imbalance, giving rise to introduction of taxonomy of species of animals, plants, fungi, bacteria and viruses (Keller *et al*., 2011) as well as heavy metals and poly-aromatic hydrocarbons. Ships make use of ballast water during transportation and release or discharge it before loading in goods. It is important to ascertain the physiochemical characteristics of ballast water for its harmful effect on aquatic lives and humans in particular. These physiochemical parameters are pH, salinity, dissolved oxygen (DO), biochemical oxygen demand (BOD), heavy metals and poly-aromatic hydrocarbons (Govind and Madhuri, 2014; Gamaha *et al*., 2021).

In overcoming harmful effect of ballast water, in 2004, the international convention for the control and management of ballast water in ships and sediment was adopted for a healthy and safe environment (Gonçalves and Gagnon 2012; Werschkun *et al.,* 2014; Stehouwer *et al*., 2015), however the effect of ballast water on physiochemical properties of water discharge into the environment was considered by few. The convention stipulated ballast water discharged performance of two types: D1 standard for exchange if water specifies 95% volumetric exchange or when using the pump, pumping through three times the volume of each tank; and D2 standard for treatment of ballast water, the maximum concentration of organisms are specified (IMO, 2004). D1 mechanism uses mechanical, chemical and physical method in exchange of ballast water in coastal or open pumping three time the volume of water in each tank; while the D2 standard for treatment of ballast water specifies the maximum amount of viable organisms allowed to be discharged, including specified harmful microbes to human health (IMO, 2004). The International Marine Organization (IMO) require ships to treat their ballast water to prevent spread of harmful aquatic organisms and pathogens whose survival depends to a large extent on physiochemical properties of water. It require ships to manage their ballast water to prevent spread of harmful aquatic organisms and pathogens, but the physiochemical properties of water was not considered, despite the fact that the survival of these organisms depend to a large extent on these parameters.

The conventional methods of treating municipal and industrial applications are used in treating ballast water but are constraint by cost, efficacy and space with IMO (2004) standard. The type of systems of ballast water treatment are solid-liquid separation and disinfection, however this methods are limited also by power and retrofitting capacities and installation cost and time (IMO, 2016). Several methods like Fenton process or ultrafiltration, reverse osmosis etc have been used. These are energy consuming and require skilled personnel. In this dispensation, adsorption is a promising method usually applied in water treatment. It depends on the nature of the adsorbents such as clays, biomass, bio-products have all been used. Clays have been used based on their abundance, requiring simple pre-treatment and preparation, surface area, hydroxyl groups, and ionic exchange which relies on electrostatic attraction between positively charged metals cations and negatively charged surface of the clay. This contribute to the immobilization of heavy metals and other pollutants in the structure of adsorbents (clay) improving the quality of the treated water.

Current ballast water treatment methods often rely on chemical or physical processes, which may have limitations in terms of efficiency and environmental impact. Kaolin clay offers a promising alternative due to its natural abundance, cost effectiveness and environmentally friendly characteristics.

The introduction of kaolin aluminosilicate clay in ballast water treatment systems can contribute to more efficient and effective ballast water treatment, which is crucial for preventing the transfer of invasive species, pollutant and pathogens through discharge of ballast water into the sea ocean. It can help meet regulatory requirements and ensure environmental protection in marine eco-system. This study is aimed at designing a simple, technological, low-energy consuming and cost effect system of clay and sharp sand to ease water flow through the clay mineral in ballast water treatment.

2.0 MATERIALS AND METHODS

2.1 Study Area

Earth (Kaolin) clays were dug from Ikpeshi in Akoko-Edo Local Government Area of Edo State, lying on latitude $7^0$17’0’ N and longitudes $6^0$6’0’E using geological plastic hammer and chisel, as described by Oyedoh *et al.*(2023). It was air-dried, pulverized and sieved with 100µm sieve. The sieved samples were stored in dry polyethene bags until they were used for the study and were coded (Ikp). Sharp sand was collected from Ethiope East River at Abraka lying between latitude $05^0$45” and $05^0$5” N and longitude 06^0 and 06^0 15’ E. They were carefully washed under running tap water to remove dirt and finally washed with distilled water. Ballast water was collected from vessels in Koko town, headquarter of Warri North Local Government Area of Delta State, Nigeria lying between latitude 6^0‘00 $006^{0'}$00 and longitude $5^0$27ˊ $59^0$99ˊ E. It is known for its natural resources, situated off busy Benin-Sapele expressway.

Graduated plastics containers of height 80 cm with diameter of 20 cm were set up, with its base packed with glass wool to about 5 cm. mixed quantities of clay/sharp sand were mixed in ratio of 2:1 and carefully loaded into the containers to 60 cm mark, ballast water was passed through it and the physiochemical and bacterial count parameters analyzed. The percolation study was carried out to examine the contact time of ballast water on the percolating medium. The clay and sharp was packed in the column of plastic vat to the adopted length 60cm based on ratio 2:1 (clay: sand) with ballast water introduced from a pressure head aspirator(container).The time for the first and 100ml was noted with performance in triplicates.

Percolation rate $= \frac{\pi d^2 m3/s}{4t}$
t = time taken to obtain drops of liquid (sec)
d = diameter of the column (m)
h = height of the column (m)

2.2 Analysis

X-ray diffractometer Phillips P/W 1800 powder diffractometer peak with in-built standard was used for mineralogical analysis. Samples collected from the field were air-dried and representative quarter of it was obtained. 2.5 g of the pulverized samples were mixed with sodium based coagulant smeared to a thin layer into the x-ray diffractioner, and later heated to 350°C for 2 mins to burn of friable substances. The sample was tested and the peaks showed less more prominence due to interruption. The diffractometer with in-built standard detector cross match the peaks and came out with mineral constituents using the XSPEX version 5.62. The deciphering of the peaks and minerals content of powdered mineral follow Bragg’s Law.

2.3 Geochemical Analysis

1g of air-dried clay sample was digested gently using prepared mixture of analytical grade of concentrated hydrofluoric (HF), hydrochloric acid (HCl) and perchloric acid ($HClO_4$) in ratio (3:2:1). It was digested on a hot plate in a flame chamber until a clear solution was obtained, cooled, filtered and made to 250 ml mark with distilled water. Elemental analysis was done with Atomic Absorption Spectrophotometer (spectrally) GBS science and structural water as loss of ignition after heating the dried sample on a muffle furnace at 1100°C for 4hrs.

2.4 Cation Exchange Capacity

About 5 g of clay air-dried sample was weighed into 250 ml Erlenmeyer flask and 30ml sodium acetate (pH 7.0) solution was added. It was covered with a stopper made of rubber and agitated on a mechanical shaker for one hour. It was transferred to a Buchner funnel fitted with a moist Whatman No 42 filter paper, using gence suction. The residue was leached at four different times using 15ml of sodium acetate solution. The flask was removed and replaced with a clean one. Exchange sodium was leached five times with 20ml portion of 1m ammonium acetate at pH 7. This was used for sodium determination.

Temperature was measured on site using mercury in glass thermometer (136model British standard model SC). pH with pH meter, HQ 20 electrical conductivity using EQ-550 conductivity meter/HACH, CENSION 5, dissolved oxygen using Winkers method and HACH method, total alkalinity by titration method with EDTA. Salinity was done using conductivity meter CENSION 5. Phosphate using colourimetric method with UV-visible spectrophotometer HACH DR 2010, total dissolved solids by HACH 2100P turbidimeter, all of which are standard methods (APHA 2017). Total bacterial count was done using the method described by Ademoroti (1996), while total petroleum hydrocarbons were determined using gas chromatography (Agilent 0890 series 4).

Ballast water samples were collected from two ships above and below the surface for five weeks in 15 liters containers. Temperature, pH and dissolved oxygen were done on site. They were then refrigerated and stored at 4°C until analysis in accordance with APHA standard methods (APHA, 2017). Poly-aromatic hydrocarbons were carried out according to Akinyinka *et al.* (2023). About 5 mg/l of ballast water sample was homogenized with Na_2SO_4 and transferred to a Soxhlet with 100 ml of hexane and dichloromethane in 1:1 for 15hrs, evaporated and purified by solid extraction with 2 g of aluminum oxide, and the upper part decanted. The PAHs were eluted with 10ml hexane, 5 ml of hexane+ dichloromethane (9:1) and 10 ml of hexane + dichloromethane (4:1).Eluted fractions were evaporated to 1 mL and used for PAHs determination in gas chromatography equipped with HPS, cross-linked with siloxane and flame ionization detector (FID) with helium gas as carrier. Initial temperature of 100°C and finally raised to 310°C at a rate of 4°C/min. Working conditions, the initial temperature of GC oven was 45°C with 2-min holding time. It was raised to 240°C with gradient rate of 150°C/min and injector temperature 280°C. After injecting samples, it was allowed to a maximum temperature of 300°C, while detector temperature was 340°C and carrier gas used was helium, pressure program at 140 psi with the volume of injection of 1.00 μL. The diffraction pattern was obtained with the help of computer and the 2O, d-values and peak intensities yielded by the powered patterns were used to identify the minerals.

3.0 RESULTS AND DISCUSSION

Table 1. Clay percentage composition, mineralogy (%) mean values

Clay minerals	**Ikp clay**
Saponite	8.90
Montmorillonite(smectite)	27.10
Chlorite	Nil
Illite	20.10
Mixed layer of illite and montmorillonite	11.00
Kaolinite	28.20
Quartz	10.50
Hematite	3.20
Total composition (%)	100

From the clay studied, kaolinite had the highest (predominant) composition of 28.20%, followed by montmonnollite (27.10%), illite (20.10%), saponite (8.90%), mixed layer (11.00%), quartz (10.50%) and hematite (3.20%). The result shows the clay to be kaolin clay type with kaolin being the highest of all the percentages.

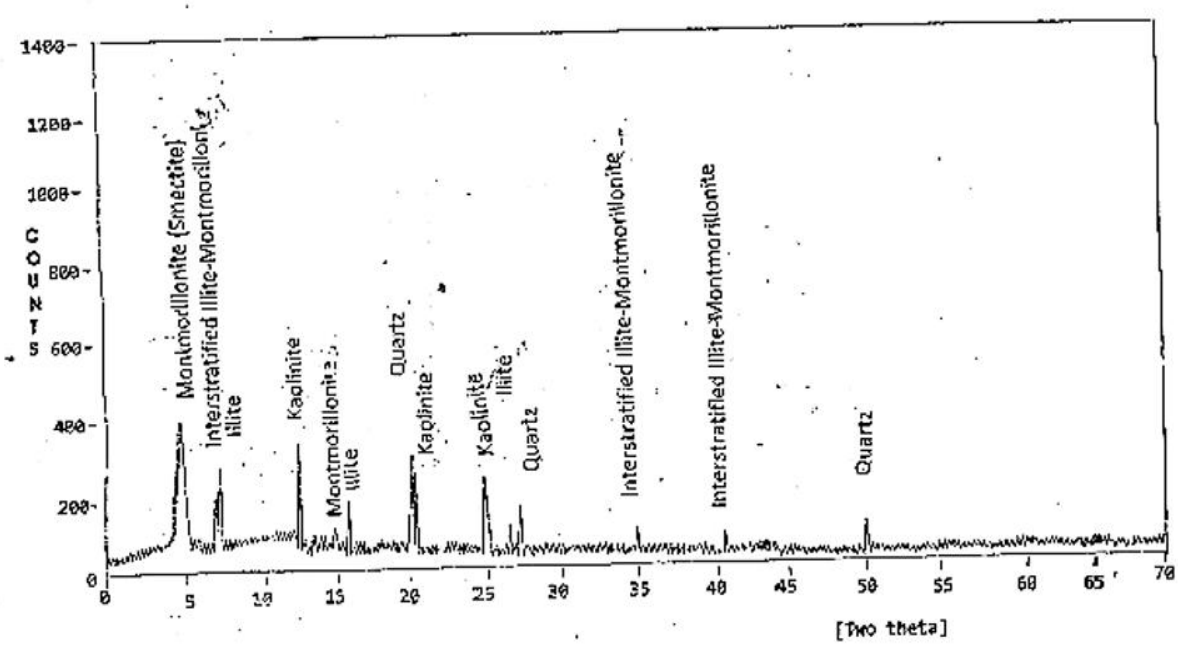

Figure 1: X-ray diffratogram of IKP clay

Table 2. Geochemical analysis of clay

% oxide	Ikp clay
SO_2	44.37
Al_2O_3	37.60
Fe_2O_3	5.61
Na_2O_3	2.97
MgO	2.93
K_2O	1.69
TiO_2	0.89
CaO	0.41
H_2O	3.35

Ikpclay analysis geochemical studies showed it contained Al_2O_3 and SiO_2 mainly. The chemical impurities (Na_2O and TiO_2) were relatively low since the aluminum content of the clay minerals was high in kaolinite clay. They are aluminosilicate clay as shown from Table 2.

Table 3. Cation exchange capacity(CEC) and percolation rate

Sample of clay	CEC(cmol/kg)	Time to obtain first drop m^2/(s)^1	Time to collect 100ml m^2/(s)^1
Ikp	81.00	8.80×10^{-8}	6.80×10^{-8}

Cation exchange capacity was 81.00cmoll/kg, this is in line to the constituents of the clay minerals found in clay samples (mixed layer), these are 2:1 clay types, their exchange capacity usually is between 80-120 Cmol/kg (Grim, 1968).The percolation rate was high, 6.80×10^{-8} m2/s, clays containing smectite usually have high percolation rate.

Table 4. Physicochemical characteristics of water (ballast water)/bacteria count (mean values)

Characteristics	Unit	Raw values	After Treatment
pH		5.31	7.9
EC	μs|cm	1,309,000	342.01
DO	mg/L	2.42	6.30
TA	mg/L	25.21	8.1× 10
Salinity	0/00	45.31	30.08
N	mg/L	7.32	0.41
P	mg/L	4.21	1.39l
TB	mg/L	24.03	4.3x10
TDS	mg/L	350	5.2×3
TH	mg/L	37.32	4.5×81
Ni	mg/L	0.09	ND

Table 4 (contd.). Physicochemical characteristics of water (ballast water)/bacteria count (mean values)

Characteristics	Unit	Raw values	After Treatment
Pb	mg/L	D001	ND
Zn	mg/L	2.30	0.51
Bacteria count	cfu	5.8×10^7	1.2×10^3

Key: EC: electrical conductivity, DO: dissolved oxygen, TA: total alkanility, TH: total hardness, N: nitrates, P: phosphorus, TB: turbidity, TDS: total dissolved solids, TH: total hardness.

The total balance of an ecosystem depend on the pH for most aquatic organisms, pH of 6.6-9.0 is required for their survival (Salahuddin, 2023) electrical conductivity was high 1,309,000 which is toxic to aquatic lives growth. Dissolved oxygen was low (2.42 mg/l) which is an indication of pollution, its recommend values is 5 mg/l and above is the accepted valued for water (NESREA, 2010). Total alkalinity of 25.21 mg/l which is not for the sustainability of aquatic lives, after treatment with clay it was increased to 8.1× 10 mg/l, values of 20 mg/l and above is considered good for aquatic lives. Total hardness was 37.32 mg/l, after treatment, it decreased to 4.5× 81, salinity of seawater is 35.0/00, that in ballast water was higher than the environment (Ghods *et al.*, 2017). Nitrate level was 7.32 mg/l, level above 0.75 mg/l is stressful to aquatic lives while above 5 mg/l is toxic, post treatment gave a reduction to 0.41 mg/l total dissolved level after treatment was good for aquatic lives 5.23 mg/l, turbidity was decreased from 24.03 mg/l to 4.3× 10 mg/l, which favours the growth of fishes especially.

The heavy metals studied were all at lower concentrations except zinc. It could be as a result of zinc used in lining (walls) the body of the vessel (ship) to prevent corrosion (Al Mukaimi *et al.*, 2018). The bacteria count was high before treatment and was reduced in post treatment (Altug *et al.*, 2012), Further disinfection could be carried out to kill the pathogens presents in ballast water.

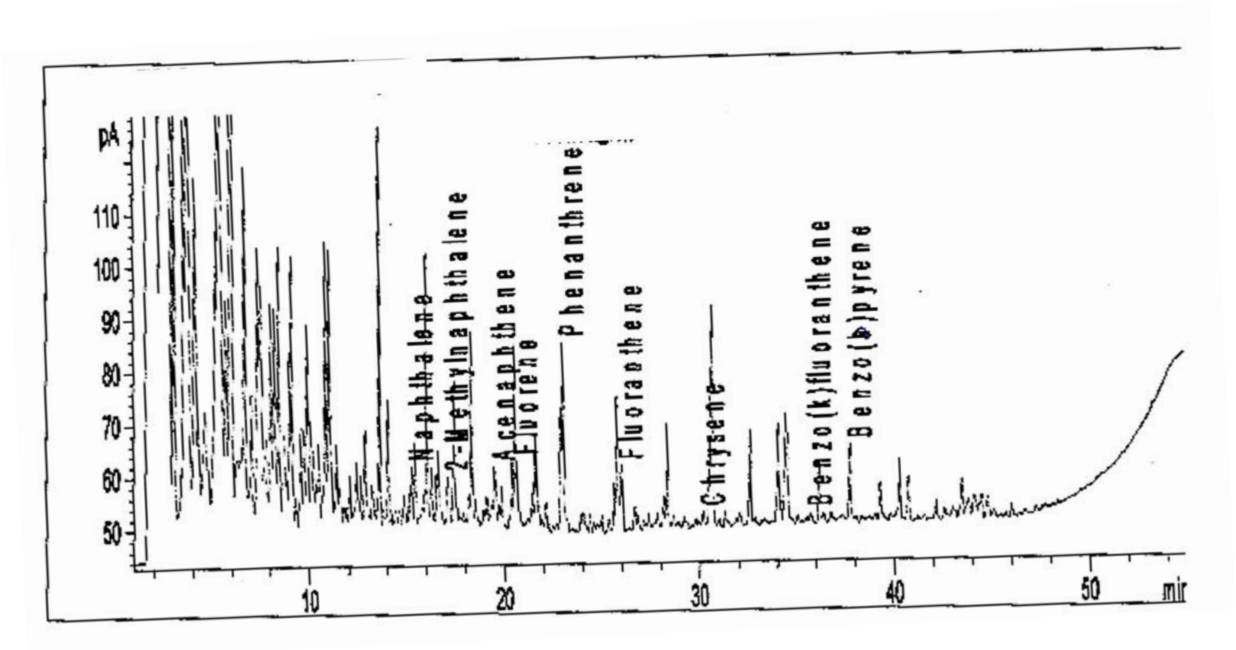

Figure 2: Chromatogram of the Polyaromatic Hydrocarbons present in ballast water.

Ballast water was also analyzed for its polyaromatic hydrocarbons and the results are presented below.

Table 5. Ballast water Polyaromatic Hydrocarbon content mean (values).

Component	Raw Value (ppm)	Post Treatment (ppm)
Napthalene	0.43	0.01
2-methyl Naphthalene	0.31	ND
Acenaphthalene	0.72	0.12
Fluorene	0.61	ND
Phenanthrene	0.12	ND
Anthracene	ND	ND
Fluoranthene	0.48	0.15
Pyrene	ND	ND
Benzo(a) Anthrene	ND	ND
Acenaphthylene	ND	ND
Chrysene	0.04	ND
Benzo(b), Pyrene	0.15	ND
Benzo(k) Fluoranthrene	0.21	0.1
Indenol (1,2,3) (d) Pyrene	ND	ND
Dibenzo (ab) Anthracene	ND	ND
Benzo (g,h,i) Perylene	ND	ND
Benzo (b) fluoranthene	ND	ND

The result of pre and post treatment is as presented above in Table 5. Phenathrene was 0.12 ppm from vessels carrying crude oil, which is a source pollution with coal tar used as ship sealants. Fluorene 0.61 ppm, chrysene at 0.04 were discharge into oceans/seas beyond its limit, naphthalene was how compared the study of 0.43 ppm in comparison with Olayinka*et al.* (2019). Some of the high molecular weight were not detected except benzo(a)pyrene and benzo(k)fluoranthene in the ballast water, and this could be as a result of the burning of petroleum (fuel). From the results, the raw ballast water is not safe to be discharged into the environment (Umudi and Umudi, 2021) since it could be bio-accumulated through food chain.

The property of ion exchange in clay is of fundamental importance in clay mineral investigation, since it influences the properties of the material in clay (Oladoja and Imohimi, 2005). Clays have broken bonds around the edges the silica alumina units giving rise to unsatisfied charges, which increases as particle size decreases, substitution within the lattice of trivalent aluminum and ions of lower valence resulting in unbalanced charges or hydrogen of exposed hydroxyl groups replaced by cation, which would be exchangeable. This high surface areas of clays and cation exchange capacity have placed them colloidal particles as adsorbent and their mineral constituent (Angita *et al.*, 2024).

4.0 CONCLUSION

The performance of the clay showed it has high potential for the treatment of ballast water. The application has the ability to reduce pollutants in ballast water. Clays can remove metals, poly-aromatic hydrocarbons, microbes and improve the quality of ballast water to be discharged into the ocean, and this quality of clay can be linked to its mineral composition. Clay is a useful adsorbent for cleaning and treating ballast water. The study shows that the concentration of pollution parameters or contaminants of ballast water can be reduced after treatment with clay.

5.0 FUNDING

None

7.0 DECLARATION OF CONFLICT OF INTEREST

None

8.0 AUTHOR'S CONTRIBUTIONS

UQE designed the study and statistical analysis, UOP collected samples and draft the manuscript, NE did sample analysis and result computation.

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